

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 087 006 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
28.03.2001 Bulletin 2001/13

(51) Int Cl.7: **C09K 11/06**, H05B 33/14,
C08K 5/3415, C07D 487/04,
C09B 57/00

(21) Application number: **00810848.2**

(22) Date of filing: **19.09.2000**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Otani, Junji
Kobe-shi, Hyogo 657-0016 (JP)
• Yamamoto, Hiroshi
Takarazuka-shi, Hyogo 665-0864 (JP)
• Dan, Norihisa
Kyoto-shi, Kyoto 612-8492 (JP)
• Iqbal, Abul
1732 Arconciel (CH)
• Moretti, Robert
1213 Petit-Lancy (CH)

(30) Priority: **27.09.1999 EP 99810868**

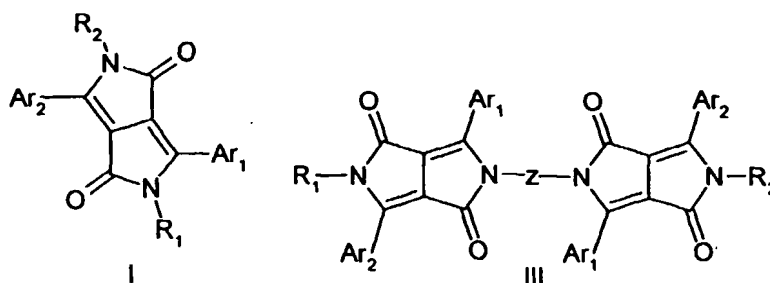
(71) Applicant: **Ciba Specialty Chemicals Holding Inc.**
4057 Basel (CH)

(54) **Electroluminescent devices comprising diketopyrrolopyrroles**

(57) Electroluminescent device comprising in this order

- (a) an anode
- (b) a hole transporting layer
- (c) a light-emitting layer
- (d) optionally an electron transporting layer and
- (e) a cathode

and a light-emitting substance, wherein the light-emitting substance is a diketopyrrolopyrrole represented by formula I or formula III

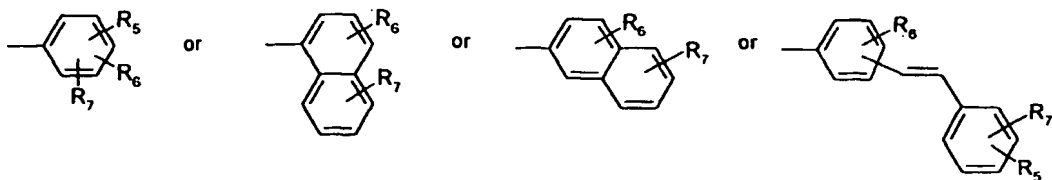


wherein R_1 and R_2 , independently from each other, stand for C_1 - C_{25} -alkyl, allyl which can be substituted one to three times with C_1 - C_3 alkyl or Ar_3 , or $-CH_2R_4-(CH_2)_m-Ar_3$, wherein R_3 and R_4 independently from each other stand for hydrogen or C_1 - C_4 alkyl, or phenyl which can be substituted one to three times with C_1 - C_3 alkyl,

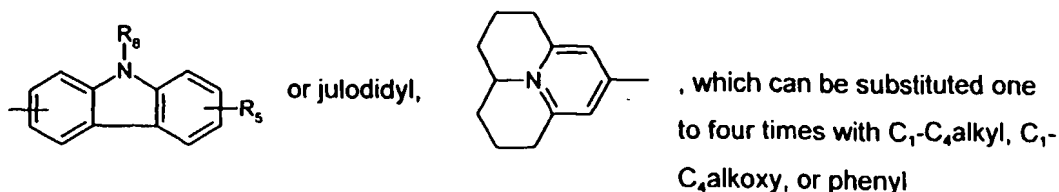
Ar_3 stands for phenyl or 1- or 2-naphthyl which can be substituted one to three times with C_1 - C_8 alkyl, C_1 - C_8 alkoxy, halogen or phenyl, which can be substituted with C_1 - C_8 alkyl or C_1 - C_8 alkoxy one to three times, and m stands for 0, 1, 2, 3 or 4,

Ar_1 and Ar_2 , independently from each other, stand for aryl radicals, preferably for

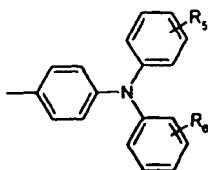
EP 1 087 006 A1



or



or



wherein

R_5 , R_6 and R_7 , independently from each other, stand for hydrogen, cyano, halogen, C_1 - C_6 alkyl, $-NR_8R_9$, $-OR_{10}$, $-S(O)_nR_8$, $-Se(O)_nR_8$, or phenyl, which can be substituted one to three times with C_1 - C_8 alkyl or C_1 - C_8 alkoxy,

wherein R_8 and R_9 , independently from each other, stand for hydrogen, phenyl, C_1 - C_{25} alkyl, C_5 - C_{12} cycloalkyl, $-CR_3R_4-(CH_2)_m-Ph$, R_{10} , wherein R_{10} stands for C_6 - C_{24} aryl, or a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein Ph, the aryl and heterocyclic radical can be substituted one to three times with C_1 - C_8 alkyl, C_1 - C_8 alkoxy, or halogen, or R_8 and R_9 stand for $-C(O)R_{10}$, wherein R_{11} can be C_1 - C_{25} alkyl, C_5 - C_{12} cycloalkyl, R_{10} , $-OR_{12}$ or $-NR_{13}R_{14}$, wherein R_{12} , R_{13} , and R_{14} stand for C_1 - C_{25} alkyl, C_5 - C_{12} cycloalkyl, C_6 - C_{24} aryl, or a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein the aryl and heterocyclic radical can be substituted one to three times with C_1 - C_8 alkyl or C_1 - C_8 alkoxy, or $-NR_8R_9$ stands for a five- or sixmembered heterocyclic radical in which R_8 and R_9 together stand for tetramethylene, pentamethylene, $-CH_2-CH_2-O-CH_2-CH_2-$, or $-CH_2-CH_2-NR_5-CH_2-CH_2-$, preferably $-CH_2-CH_2-O-CH_2-CH_2-$, and n stands for 0, 1, 2 or 3,

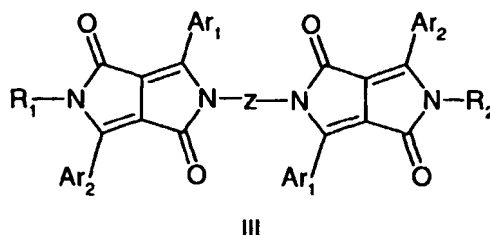
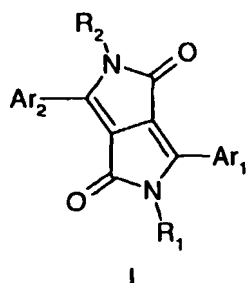
and wherein Z stands for a diradical selected from the group consisting of a single bond, C_2 - C_6 alkylene, which can be substituted one to three times with C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or phenyl, phenylene or naphthylene, processes for the preparation of compounds I, its uses and compositions comprising the compounds I and/or III.

Description

[0001] The present invention relates to an electroluminescent device comprising in this order

- (a) an anode
- (b) a hole transporting layer
- (c) a light-emitting layer
- (d) optionally an electron transporting layer and
- (e) a cathode

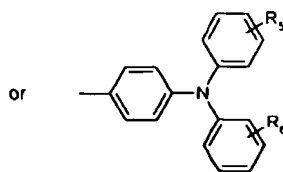
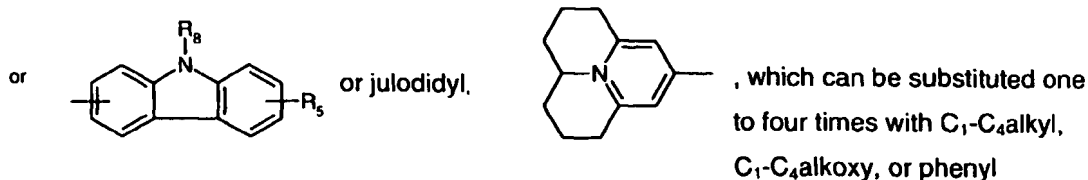
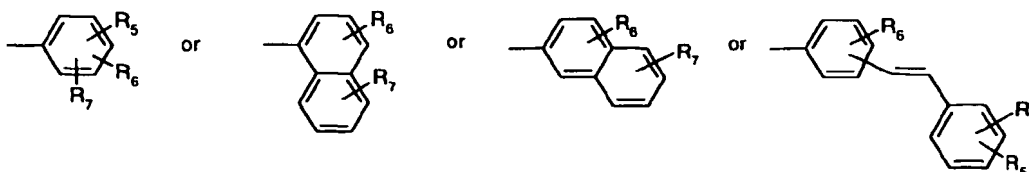
and a light-emitting substance, wherein the light-emitting substance is a diketopyrrolopyrrole ("DPP") represented by formula I or formula III



wherein R₁ and R₂, independently from each other, stand for C₁-C₂₅-alkyl, allyl which can be substituted one to three times with C₁-C₃alkyl or Ar₃, or -CH₂R₄-(CH₂)_m-Ar₃, wherein R₃ and R₄ independently from each other stand for hydrogen or C₁-C₄alkyl, or phenyl which can be substituted one to three times with C₁-C₃ alkyl,

Ar₃ stands for phenyl or 1- or 2-naphthyl which can be substituted one to three times with C₁-C₈alkyl, C₁-C₈alkoxy, halogen or phenyl, which can be substituted with C₁-C₈alkyl or C₁-C₈alkoxy one to three times, and m stands for 0, 1, 2, 3 or 4,

Ar₁ and Ar₂, independently from each other, stand for aryl radicals, preferably for



wherein

R_5 , R_6 and R_7 , independently from each other, stand for hydrogen, cyano, halogen, C_1 - C_6 alkyl, $-NR_8R_9$, $-OR_{10}$, $-S(O)_nR_8$, $-Se(O)_nR_8$, or phenyl, which can be substituted one to three times with C_1 - C_8 alkyl or C_1 - C_8 alkoxy,

wherein R_8 and R_9 , independently from each other, stand for hydrogen, phenyl, C_1 - C_{25} alkyl, C_5 - C_{12} cycloalkyl,

$-CR_3R_4-(CH_2)_m-Ph$, R_{10} , wherein R_{10} stands for C_6 - C_{24} aryl, or a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein Ph, the aryl and heterocyclic radical can be substituted one to three times with C_1 - C_8 alkyl, C_1 - C_8 alkoxy, or halogen, or R_8 and R_9 stand for $-C(O)R_{10}$, wherein R_{11} can be C_1 - C_{25} alkyl, C_5 - C_{12} cycloalkyl, R_{10} , $-OR_{12}$ or $-NR_{13}R_{14}$, wherein R_{12} , R_{13} , and R_{14} stand for C_1 - C_{25} alkyl, C_5 - C_{12} cycloalkyl, C_6 - C_{24} aryl,

or

a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein the aryl and heterocyclic radical can be substituted one to three times with C_1 - C_8 alkyl or C_1 - C_8 alkoxy, or $-NR_8R_9$ stands for a five- or sixmembered heterocyclic radical in which R_8 and R_9 together stand for tetramethylene, pentamethylene, $-CH_2-CH_2-O-CH_2-CH_2-$, or $-CH_2-CH_2-NR_5-CH_2-CH_2-$, preferably $-CH_2-CH_2-O-CH_2-CH_2-$, and n stands for 0, 1, 2 or 3, and wherein Z stands for a diradical selected from the group consisting of a single bond, C_2 - C_6 alkylene, which can be substituted one to three times with C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or phenyl, phenylene or naphthylene.

[0002] Thin film type electroluminescent devices usually consist essentially of a pair of electrodes and at least one charge transporting layer in between. Usually two charge transporting layers, a hole transporting layer (next to the anode) and an electron transporting layer (next to the cathode) are present. Either one of them contains - depending on its properties as hole-transporting or electron-transporting material - an inorganic or organic fluorescence substance as light-emitting material. It is also common, that a light-emitting material is used as an additional layer between the hole-transporting and the electron-transporting layer.

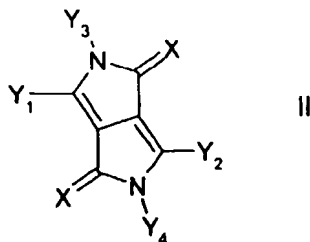
[0003] It is presently common to prepare organic electroluminescent ("EL") devices which contain an organic fluorescent substance by a vacuum evaporation process, e.g. described in Appl. Phys. Lett., 51, 913 (1987). In general, two types of such vacuum evaporation processes are applied according to the constitution of light emitting material: a one-component type process and a two-components type (or "Host-Guest type" or "binary system") process (e.g. described in J. Appl. Phys., 65, 3610 (1989)).

[0004] For emitting a light of red, green or blue color in a one-component system, the light emitting materials themselves have to emit an intense fluorescence of red, green or blue color. Further, a vacuum evaporation process has to give a deposited film of uniform quality, and the film thus formed has to be endowed with appropriate ("carrier") mobility for positive holes and/or electrons i.e. properties of a semiconductor.

[0005] Numerous materials emitting light in the green- or blue-colored region are known.

[0006] JP-B2 2,749,407 (Pioneer Electron Corp. & Nippon Kayaku Co. Ltd.) describes as a light emitting material N, N'-bis(2,5-di-tert.-butylphenyl)-3,4,9,10-peryleneedicarboximide. However, its luminance is as low as 27 cd/m², which is insufficient for commercial applications.

[0007] JP-A2 2,296,891 (Ricoh) claims an electroluminescent element comprising a positive electrode, a negative electrode and one organic compound layer or a plurality of organic compound layers held between the positive and negative electrodes, but no hole transporting substance. At least one layer of said organic compound layers is a layer containing a pyrrolopyrrole compound represented by the following formula II



wherein Y_1 and Y_2 independently from each other represent a substituted or unsubstituted alkyl, cycloalkyl or aryl group, Y_3 and Y_4 independently represent a hydrogen atom or a substituted or unsubstituted alkyl or aryl group, and X represents an oxygen or a sulfur atom. Only four compounds are mentioned explicitly, namely wherein X stands for oxygen in all cases, and wherein (a) $Y_3 = Y_4 = \text{methyl}$ and $Y_1 = Y_2 = \text{p-tolyl}$, (b) $Y_3 = Y_4 = \text{methyl}$ and $Y_1 = Y_2 = \text{hydrogen}$, (c) $Y_3 = Y_4 = \text{hydrogen}$ and $Y_1 = Y_2 = \text{p-tolyl}$, and (d) $Y_3 = Y_4 = \text{hydrogen}$ and $Y_2 = \text{p-chlorophenyl}$. However,

according to JP-A2 5,320,633 (see below), a follow-up study of the same inventors revealed that an emission of light is only observed, if the DPP-compounds II are used together with other compounds. This observation is supported by comparative example 2 of JP-A2 5,320,633, which shows that no emission is observed, if DPP II is used alone, i.e. without the addition of tris(8-hydroxyquinolino)aluminium ("Alq₃").

[0008] JP-A2 5,320,633 (Sumitomo) claims an organic EL device having a light emitting layer comprising a light emitting material in an amount of 0.005 to 15 parts by weight of a DPP-compound between a pair of electrodes, wherein at least one electrode being transparent or semi-transparent. Although the main claim is silent about the use of Alq₃, it is clear from the specification and the examples, especially from comparative example 2, that Alq₃ is an essential feature in the claimed EL element or device.

[0009] JP-A2 9003448 (Toyo Ink) claims an organic EL element having between a pair of electrodes a luminous layer containing a DPP-compound as electron-transporting material or an organic compound thin film layer including a luminous layer and an electron-injecting layer wherein the electron-injecting layer contains a DPP compound as the electron-transporting material. In addition, another EL element further comprising a hole-injecting layer is claimed. The disadvantage of the claimed EL devices is that according to the examples always Alq₃ and a phenanthrene diamine (as hole-injecting material) have to be used.

[0010] EP-A 499,011 claims an organic EL element comprising a DPP compound, however, only systems having no electron-transporting layers are verified. Further, only highly crystalline organic pigments should be employed for a light emitting material. However, one of the requirements for light emitting materials is its morphological stability. Crystalline materials show a tendency to be morphologically modulated in the evaporated film. This becomes a disadvantage for ensuring device durability.

[0011] Usually in Host-Guest type light emitting materials, the sensitized fluorescence caused by the Förster type excitation energy transfer from Host to Guest is utilized. Accordingly, in addition to the abovementioned conditions, it is also important for this type of materials to fulfill the condition that the fluorescent spectrum of the Host in the solid state overlaps with the light absorption spectrum of the Guest in the solution state.

[0012] As to green-colored light emission, so high an EL emitting efficiency as >10 lm/W is achieved by using Alq₃ as Host and a quinacridone derivative as Guest. Such a system is used in practice in monocolour displays.

[0013] With regard to blue-colored light emission, Appl. Phys. Lett., 67, 3853 (1995) reports that a high EL emitting efficiency of 1.5 lm/W can be achieved by using a distyryl derivative as Host and an amino-substituted distyryl derivative as Guest. As above, the Guest material is not required to have a high carrier mobility, and therefore not required to be a semiconductor.

[0014] Many of the known orange-, red- or yellow-colored fluorescent dyes for use as dyestuff laser have a high fluorescence quantum yield in the solution state. Their Stokes shift, however, is generally small. That is, most of the yellow-, orange- or red-colored fluorescent dyes absorb yellow, orange or red light in the solution state and emit a yellow-, orange- or red-colored fluorescence. Accordingly, if a yellow-, orange- or red-colored fluorescent dye is considered as Guest, the Host material should be a material emitting a yellow-, orange- or red-colored fluorescence in the solid state, as designated by the conditions necessary for realization of a sensitized fluorescence through Förster type excitation energy transfer.

[0015] Further, compatibility with the Guest must also be taken into account in addition to the conditions similar to those required of one-component type light emitting materials. In conclusion, the Host material must be a yellow-, orange- to red-colored solid fluorescent material in order to realize a yellow-, orange- or red-colored organic EL luminescence in a two-components system. At the present stage, however, no satisfactory yellow-, orange- or red-light emitting material is known for the same reason as in the one-component system.

[0016] EP-A 648770 describes solid fluorescent, soluble latent pigments. However, latent pigments cannot be used for the abovementioned vacuum evaporation processes because they are transformed into insoluble non-fluorescent DPP pigments upon heating.

[0017] Hence, the object of this invention was to provide electroluminescent devices emitting yellow, orange or red light, wherein organic light-emitting materials should be used fulfilling

- intense photoluminescence in the solid state for the one-component system, and/or the Host in the binary system, and in the solution state for the Guest in the binary system,
- carrier mobility for a positive hole and/or an electron,
- necessary properties for vacuum evaporation and deposition (such as ability to sublime or evaporate),
- the ability for a homogeneous film formation,
- the property of exhibiting a "pure" color,
- the ability that the electronic potential should match with the electrodes and/or with the substances adjacent to,
- compatibility of the solid host and the molecular guest in case binary systems are desired,
- high durability (thermal, electrical etc.) and morphological stability.

[0018] Accordingly, the abovementioned electroluminescent devices were found.

In addition, a process for its preparation, and new light-emitting materials were found, too.

[0019] Typical constitutions of latest organic electroluminescent devices are:

- 5 (i) an anode/a hole transporting layer/an electron transporting layer/a cathode,
in which compounds I are used either as positive-hole transport compounds, which is exploited to form the light emitting and hole transporting layers, or as electron transport compounds, which can be exploited to form the light-emitting and electron transporting layers, and
- (ii) an anode/a hole transporting layer/a light-emitting layer/an electron transporting layer/a cathode,
- 10 in which the compounds I form the light-emitting layer regardless of whether they exhibit positive-hole or electron transport properties in this constitution.

[0020] It is possible that the light-emitting layer can consist of two or more fluorescent substances of formula I for energy donor(s) and/or energy acceptor(s).

15 [0021] The devices can be prepared in several ways. Usually, vacuum evaporation is extensively used for the preparation. Preferably, the organic layers are laminated in the above order on a commercially available indium-tin-oxide ("ITO") glass substrate held at room temperature, which works as the anode in the constitutions. The membrane thickness is preferably in the range of 1 to 10,000 nm, more preferably 1 to 5,000 nm, more preferably 1 to 1,000 nm, more preferably 1 to 500 nm. The cathode metal such as Mg/Ag alloy and Li-Al binary system of ca. 200 nm is laminated on the top of the organic layers. The vacuum during the deposition is preferably less than 0.1333 Pa (1×10^{-3} Torr), more preferably less than 1.333×10^{-3} Pa (1×10^{-5} Torr), more preferably less than 1.333×10^{-4} Pa (1×10^{-6} Torr).

20 [0022] As anode usual anode materials which possess high work function such as metals like gold, silver, copper, aluminum, indium, iron, zinc, tin, chromium, titanium, vanadium, cobalt, nickel, lead, manganese, tungsten and the like, metallic alloys such as magnesium/copper, magnesium/silver, magnesium/aluminum, aluminum/indium and the like, semiconductors such as Si, Ge, GaAs and the like, metallic oxides such as indium-tin-oxide ("ITO"), ZnO and the like, metallic compounds such as CuI and the like, and furthermore, electroconducting polymers such as polyacetylene, polyaniline, polythiophene, polypyrrole, polyparaphenylene and the like, preferably ITO, most preferably ITO on glass as substrate can be used. Of these electrode materials, metals, metallic alloys, metallic oxides and metallic compounds can be transformed into electrodes, for example, by means of the sputtering method. In the case of using a metal or a metallic alloy as a material for an electrode, the electrode can be formed also by the vacuum deposition method. In the case of using a metal or a metallic alloy as a material forming an electrode, the electrode can be formed, furthermore, by the chemical plating method (see for example, Handbook of Electrochemistry, pp 383-387, Mazuren, 1985). In the case of using an electroconducting polymer, an electrode can be made by forming it into a film by means of anodic oxidation polymerization method onto a substrate which is previously provided with an electroconducting coating. The thickness of an electrode to be formed on a substrate is not limited to a particular value, but, when the substrate is used as a light emitting plane, the thickness of the electrode is preferably within the range of from 1 nm to 100 nm, more preferably, within the range of from 5 to 50 nm so as to ensure transparency.

30 [0023] In a preferred embodiment ITO is used on a substrate having an ITO film thickness in the range of from 10 nm (100 Å) to 1 μ (10000 Å), preferably from 20 nm (200 Å) to 500 nm (5000 Å). Generally, the sheet resistance of the ITO film is chosen in the range of not more than 100 Ω/cm^2 , preferred from not more than 50 Ω/cm^2 .

[0024] Such anodes are commercially available from e.g. Japanese manufacturers such as Geomatech Co.Ltd., Sanyo Vacuum Co. Ltd., Nippon Sheet Glass Co. Ltd.

45 [0025] As substrate either an electronconducting or electrically insulating material can be used. In case of using an electroconducting substrate, a light emitting layer or a positive hole transporting layer is directly formed thereupon, while in case of using an electrically insulating substrate, an electrode is firstly formed thereupon and then a light emitting layer or a positive hole transporting layer is superposed.

[0026] The substrate may be either transparent, semi-transparent or opaque. However, in case of using a substrate as an indicating plane, the substrate must be transparent or semi-transparent.

50 [0027] Transparent electrically insulating substrates are, for example, inorganic compounds such as glass, quartz and the like, organic polymeric compounds such as polyethylene, polypropylene, polymethylmethacrylate, polyacrylonitrile, polyester, polycarbonate, polyvinylchloride, polyvinylalcohol, polyvinylacetate and the like. Each of these substrates can be transformed into a transparent electroconducting substrate by providing it with an electrode according to one of the methods described above.

55 [0028] As examples of semi-transparent electrically insulating substrates, there are inorganic compounds such as alumina, YSZ (yttrium stabilized zirconia) and the like, organic polymeric compounds such as polyethylene, polypropylene, polystyrene, epoxy resin and the like. Each of these substrates can be transformed into a semi-transparent electroconducting substrate by providing it with an electrode according to one of the abovementioned methods.

[0029] As examples of opaque electroconducting substrates, there are metals such as aluminum, indium, iron, nickel,

zinc, tin, chromium, titanium, copper, silver, gold, platinum and the like, various electroplated metals, metallic alloys such as bronze, stainless steel and the like, semiconductors such as Si, Ge, GaAs, and the like, electroconducting polymers such as polyaniline, polythiophene, polypyrrole, polyacetylene, polyparaphenylene and the like.

[0030] A substrate can be obtained by forming one of the above listed substrate materials to a desired dimension. It is preferred that the substrate has a smooth surface. Even if it has a rough surface, however, it will not cause any problem for practical use, provided that it has round unevenness having a curvature of not less than 20 μm . As for the thickness of the substrate, there is no restriction as far as it ensures sufficient mechanical strength. As cathode usual cathode materials which possess low work function such as alkali metals, earth alkaline metals, group 13 elements, silver, and copper as well as alloys or mixtures thereof such as sodium, lithium, potassium, sodium-potassium alloy, magnesium, magnesium-silver alloy, magnesium-copper alloy, magnesium-aluminum alloy, magnesium-indium alloy, aluminum, aluminum-aluminum oxide alloy, aluminum-lithium alloy, indium, calcium, and materials exemplified in EP-A 499,011 such as electroconducting polymers e.g. polypyrrole, polythiophene, polyaniline, polyacetylene etc., preferably Mg/Ag alloys, or Li-Al compositions can be used.

[0031] In a preferred embodiment magnesium-silver alloy or a mixture of magnesium and silver mixture, or lithium-aluminum alloy or a mixture of lithium and aluminum can be used in a film thickness in the range of from 10 nm (100 Å) to 1 μm (10000 Å), preferably from 20 nm (200 Å) to 500 nm (5000 Å).

[0032] Such cathodes can be deposited on the foregoing electron transporting layer by known vacuum deposition techniques described above.

[0033] In a preferred embodiment of this invention a light-emitting layer can be used between the hole transporting layer and the electron transporting layer. Usually it is prepared by forming a thin film of a DPP compound of formula I on the hole transporting layer.

[0034] As methods for forming said thin film, there are, for example, the vacuum deposition method, the spin-coating method, the casting method, the Langmuir-Blodgett ("LB") method and the like. Among these methods, the vacuum deposition method, the spin-coating method and the casting method are particularly preferred in view of ease in operation and cost.

[0035] In case of forming a thin film using a DPP compound I by means of the vacuum deposition method, the conditions under which the vacuum deposition is carried out are usually strongly dependent on the properties, shape and crystalline state of the compound. However, optimum conditions can be selected for example within the range of from 100 to 400°C in temperature for the heating boat, -100 to 350°C in substrate temperature, 1.33×10^4 Pa (1×10^2 Torr) to 1.33×10^{-4} Pa (1×10^{-6} Torr) in pressure and 1 μm to 6 nm/sec in deposition rate.

[0036] In an organic EL element, the thickness of the light emitting layer thereof is one of the factors determining its light emission properties. For example, if a light emitting layer is not sufficiently thick, a short circuit can occur quite easily between two electrodes sandwiching said light emitting layer, and therefore, no EL emission is obtained. On the other hand, if the light emitting layer is excessively thick, a large potential drop occurs inside the light emitting layer because of its high electrical resistance, so that the threshold voltage for EL emission increases. Accordingly, it is necessary to limit the thickness of an organic light emitting layer within the range of from 5 nm to 5 μm . A preferable thickness is within the range of from 10 nm to 500 nm.

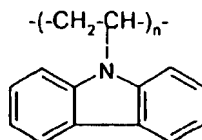
[0037] In the case of forming a light emitting layer by using the spin-coating method and the casting method, the coating can be carried out using a solution prepared by dissolving the DPP I in a concentration of from 0.0001 to 90% by weight in an appropriate organic solvent such as benzene, toluene, xylene, tetrahydrofuran, methyltetrahydrofuran, N,N-dimethylformamide, dichloromethane, dimethylsulfoxide and the like. Herein, the higher the concentration of DPP I, the thicker the resulting film, while the lower the concentration, the thinner the resulting film. However, if the concentration exceeds 90% by weight, the solution usually is so viscous that it no longer permits forming a smooth and homogenous film. On the other hand, as a rule, if the concentration is less than 0.0001% by weight, the efficiency of forming a film is too low to be economical. Accordingly, a preferred concentration of DPP I is within the range of from 0.01 to 80% by weight.

[0038] In the case of using the above spin-coating or casting method, it is possible to further improve the homogeneity and mechanical strength of the resulting layer by adding a polymer binder in the solution for forming the light emitting layer. In principle, any polymer binder may be used, provided that it is soluble in a solvent in which DPP I is dissolved. Examples of such polymer binders are polycarbonate, polyvinylalcohol, polymethacrylate, polymethylmethacrylate, polyester, polyvinylacetate, epoxy resin and the like. A solution for forming a light emitting layer may have any concentrations of DPP I, of a polymer binder and solvent. However, if the solid content composed of the polymer binder and DPP I exceeds 99% by weight, the fluidity of the solution is usually so low that it is impossible to form a light emitting layer excellent in homogeneity. On the other hand, if the content of DPP I is substantially smaller than that of the polymer binder, in general the electrical resistance of said layer is very large, so that it does not emit light unless a high voltage is applied thereto. Furthermore, since the concentration of DPP I in the layer is small in this case, its light emission efficiency is relatively low. Accordingly, the preferred composition ratio of a polymer binder to DPP I is chosen within the range of from 10:1 to 1:50 by weight, and the solid content composed of both components in the solution is

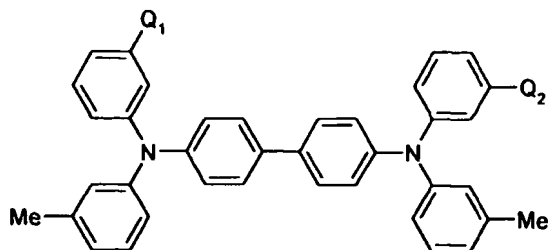
preferably within the range of from 0.01 to 80% by weight, and more preferably, within the range of about 0.1 to 60% by weight.

[0039] In the case of forming a light emitting layer by the spin-coating method or casting method, the thickness of said layer may be selected in the same manner as in the case of forming a light emitting layer by the vacuum deposition method. That is, the thickness of the layer preferably is chosen within the range of from 5 nm to 5 μ m, and more preferably, within the range of from 10 nm to 500 nm.

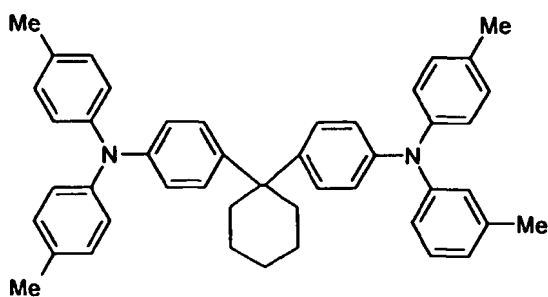
[0040] As hole-transporting layers known organic hole transporting compounds such as polyvinyl carbazole,



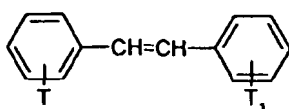
a TPD compound disclosed in J.Amer.Chem.Soc. 90 (1968) 3925



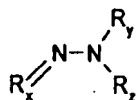
wherein Q_1 and Q_2 each represent a hydrogen atom or a methyl group;
a compound disclosed in J. Appl. Phys. 65(9) (1989) 3610



a stilbene based compound



wherein T and T_1 stand for an organic rest
a hydrazone based compound



and the like.

[0041] Compounds to be used as a positive hole transporting material are not restricted to the above listed compounds. Any compound having a property of transporting positive holes can be used as a positive hole transporting material such as triazole derivatives, oxadiazole derivatives, imidazole derivatives, polyaryalkane derivatives, pyrazoline derivative, pyrazolone derivatives, phenylene diamine derivatives, arylamine derivatives, amino substituted chalcone derivatives, oxazole derivatives, stilbenylanthracene derivatives, fluorenone derivatives, hydrazone derivatives, stilbene derivatives, copolymers of aniline derivatives, electro-conductive oligomers, particularly thiophene oligomers, porphyrin compounds, aromatic tertiary amine compounds, stilbenyl amine compounds etc. Particularly, aromatic tertiary amine compounds such as N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-4,4'-diaminobiphenyl (TPD), 2,2'-bis(di-p-torylaminophenyl)propane, 1,1'-bis(4-di-torylaminophenyl)-4-phenylcyclohexane, bis(4-dimethylamino-2-methylphenyl)phenylmethane, bis(4-di-p-torylaminophenyl)phenylmethane, N,N'-diphenyl-N,N'-di(4-methoxyphenyl)-4,4'-diaminobiphenyl, N,N,N',N'-tetraphenyl-4,4'-diaminodiphenylether, 4,4'-bis(diphenylamino)quaterphenyl, N,N,N-tri(p-tolyl)amine, 4-(di-p-torylamino)-4'-[4-(di-p-torylamino)styryl]stilbene, 4-N,N-diphenylamino-(2-diphenylvinyl)benzene, 3-methoxy-4'-N,N-diphenylaminostilbene, N-phenylcarbazole etc.

[0042] Furthermore, 4,4'-bis[N-(1-naphtyl)-N-phenylamino]biphenyl disclosed in US 5,061,569, the compounds in which three triphenylamine units are bound to a nitrogen atom like "star-burst" structure e.g. 4,4',4"-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine disclosed in EP-A 508,562.

[0043] A positive hole transporting layer can be formed by preparing an organic film containing at least one positive hole transporting material on the anode. The positive hole transporting layer can be formed by the vacuum deposition method, the spin-coating method, the casting method, the LB method and the like. Of these methods, the vacuum deposition method, the spin-coating method and the casting method are particularly preferred in view of ease and cost.

[0044] In the case of using the vacuum deposition method, the conditions for deposition may be chosen in the same manner as described for the formation of a light emitting layer (see above). If it is desired to form a positive hole transporting layer comprising more than one positive hole transporting material, the coevaporation method can be employed using the desired compounds.

[0045] In the case of forming a positive hole transporting layer by the spin-coating method or the casting method, the layer can be formed under the conditions described for the formation of the light emitting layer (see above).

[0046] As in the case of forming a light emitting layer using a solution containing a polymer binder, a smoother and more homogeneous positive hole transporting layer can be formed by using a solution containing a binder and at least one positive hole transporting material. The coating using such a solution can be performed in the same manner as in cases of forming a light emitting layer using a polymer binder. Any polymer binder may be used, provided that it is soluble in a solvent in which at least one positive hole transporting material is dissolved. Examples of appropriate polymer binders and of appropriate and preferred concentrations are given above when describing the formation of a light emitting layer.

[0047] The thickness of a positive hole transporting layer is preferably chosen in the range of from 0.5 to 1000 nm, preferably from 1 to 100 nm, more preferably from 2 to 50 nm.

[0048] As electron transporting materials for an electron-transporting layer it is preferred to have a high electron injection efficiency from the cathode and a high electron mobility. The following materials can be exemplified for electron transporting materials: tris(8-hydroxyquinolato)aluminum(III) and its derivatives, bis(10-hydroxybenzo[h]quinolinolato)beryllium(II) and its derivatives, oxadiazole derivatives such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole and its dimer systems such as 1,3-bis(4-tert-butylphenyl)-1,3,4-oxadiazolylbiphenylene and 1,3-bis(4-tert-butylphenyl)-1,3,4-oxadiazolylphenylene, triazole derivatives, phenanthroline derivatives or perylene tetracarboxylic acid derivatives such as disclosed in Appl. Phys. Lett. 48 (2) (1986) 183.

[0049] An electron transporting layer can be formed by preparing an organic film containing at least one electron transporting material on the hole transporting layer or on the light-emitting layer. The electron transporting layer can be formed by the vacuum deposition method, the spin-coating method, the casting method, the LB method and the like.

[0050] As in the case of forming a light emitting layer or a positive hole transporting layer by using a solution containing a polymer binder, a smoother and more homogeneous electron transporting layer can be formed by using a solution containing a binder and at least one electron transporting material.

[0051] The thickness of an electron transporting layer is preferably chosen in the range of from 0.5 to 1000 nm, preferably from 1 to 100 nm, more preferably from 2 to 50 nm.

[0052] Yellow to red fluorescent light-emitting compounds means that the used light-emitting compounds preferably

have a fluorescence emission maximum in the range of from 500 to 780, more preferably from 520 to 750, more preferred from 540 to 700 nm. Further, the inventive compounds preferably exhibit an absorption maximum in the range of 450 to 580 nm.

[0053] The light-emitting compounds I usually exhibit a fluorescence quantum yield ("FQY") in the range of from 1 > FQY ≥ 0.3 (measured in aerated toluene or DMF). Further, in general, the inventive compounds I exhibit a molar absorption coefficient in the range of from 5000 to 100000.

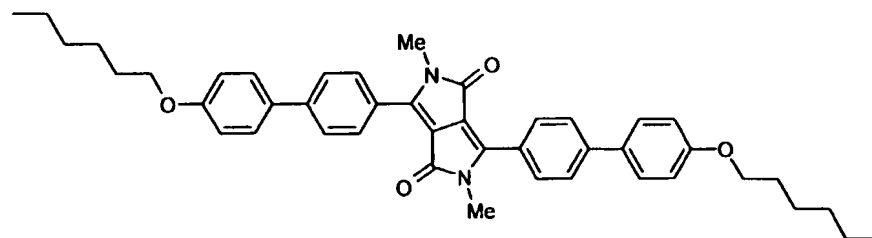
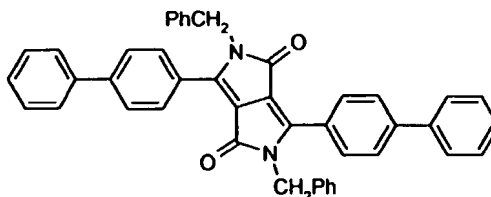
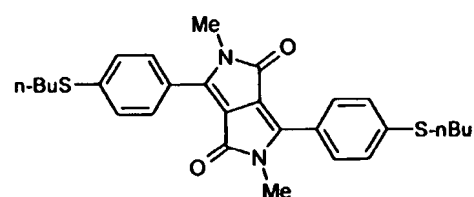
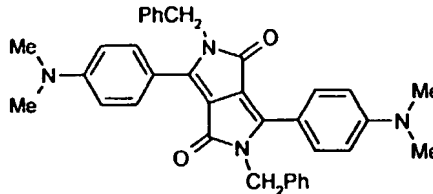
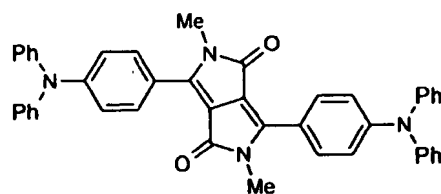
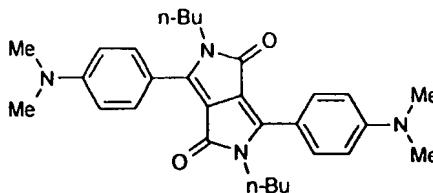
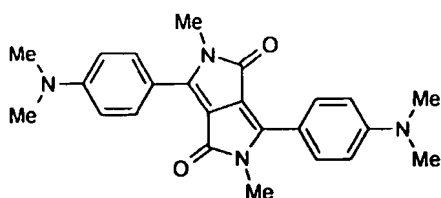
[0054] A preferred embodiment relates to DPP-compounds I, wherein $R_1 = R_2$, and $Ar_1 = Ar_2$, particularly preferred wherein in addition to the above $R_3 = R_4 = H$, $m = 0$ and $n = 0$, most preferred are DPP-compounds in which

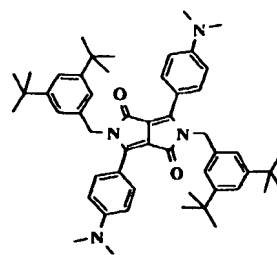
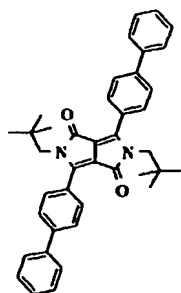
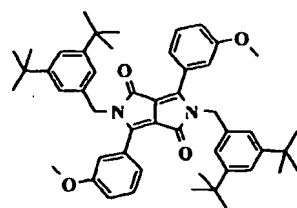
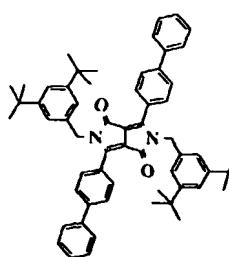
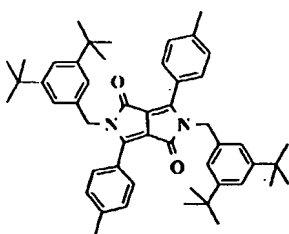
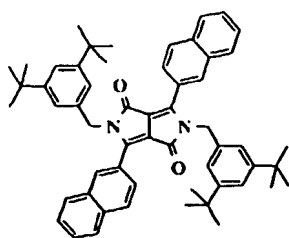
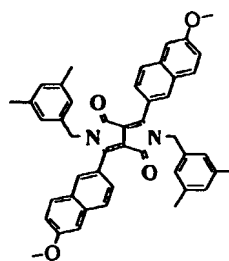
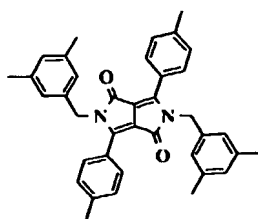
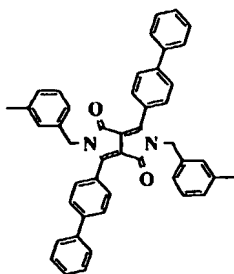
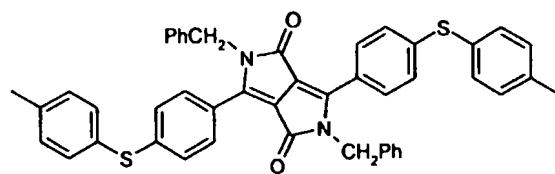
(a) $R_1 = R_2 = C_1-C_8$ alkyl, $Ar_1 = Ar_2 =$ phenyl or stilbene, $R_7 = -NR_8R_9$ in 4-position, $R_5 = R_6 =$ hydrogen, and $R_8 = R_9 = C_1-C_8$ alkyl or phenyl, or

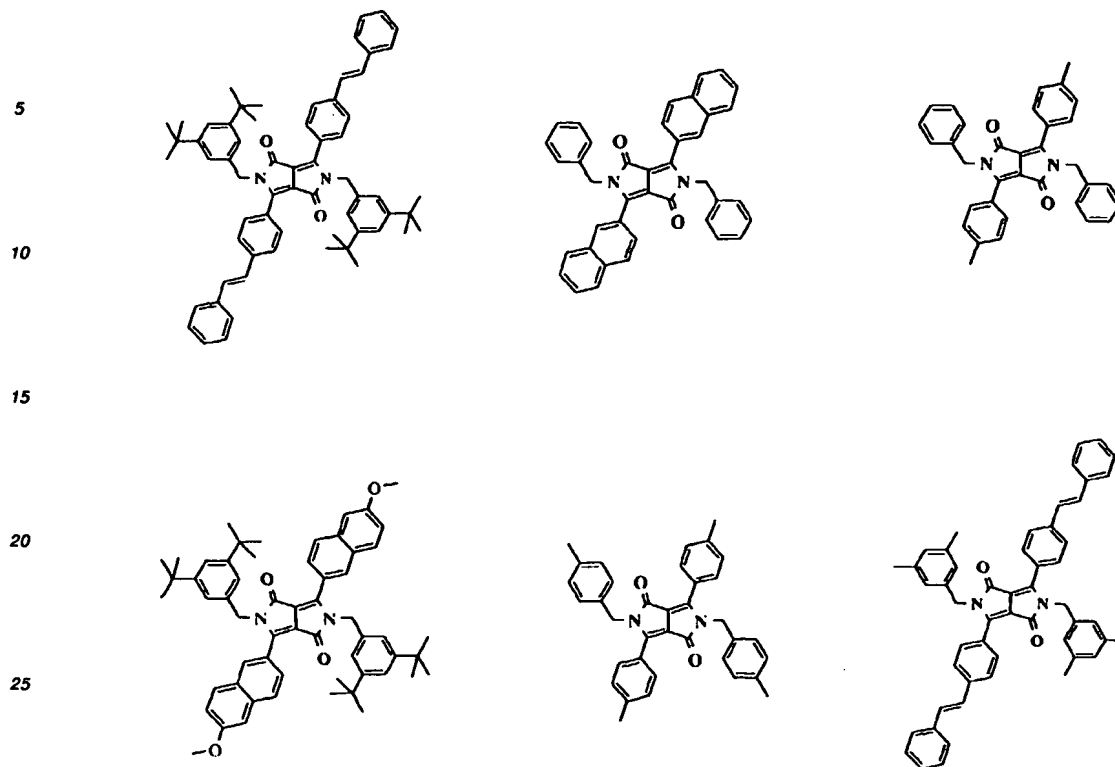
(b) $R_1 = R_2 = C_1-C_8$ alkyl, $-(CH_2)_m-Ph$, $Ar_1 = Ar_2 =$ phenyl or stilbene, $R_5 = R_6 =$ hydrogen, $R_7 = -SR_7$, $-OR_{10}$, $-N(R_8)_2$ or unsubstituted or substituted phenyl in para-position, and $R_8 = C_1-C_8$ alkyl, phenyl or a heterocyclic radical, both unsubstituted or substituted, or C_5-C_{12} -cycloalkyl, or

(c) $R_1 = R_2 = -CH_2-Ph$, wherein phenyl can be substituted with phenyl, naphthyl or C_1-C_4 alkyl up to two times, $Ar_1 = Ar_2 =$ phenyl or 1- or 2-naphthyl, $R_5 = R_6 =$ hydrogen, $R_7 =$ hydrogen or $-OMe$, in case where $Ar_1 = Ar_2 =$ 1- or 2-naphthyl, or, in all other cases, C_1-C_8 alkyl or phenyl.

[0055] Particularly preferred DPP-compounds I are the following compounds:







C₁-C₂₅alkyl is typically linear or branched - where possible - methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, heneicosyl, docosyl, tetracosyl or pentacosyl, preferably C₁-C₈alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, more preferably C₁-C₄alkyl such as typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl; C₁-C₆alkyl stands for methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethyl-propyl, n-hexyl; C₁-C₃alkyl stands for methyl, ethyl, n-propyl, or isopropyl.

[0056] C₁-C₈alkoxy is typically methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy, n-pentoxy, 2-pentoxy, 3-pentoxy, 2,2-dimethylpropoxy, n-hexoxy, n-heptoxy, n-octoxy, 1,1,3,3-tetramethylbutoxy and 2-ethylhexoxy, preferably C₁-C₄alkoxy such as typically methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, isobutoxy, tert.-butoxy.

[0057] C₆-C₂₄aryl is typically phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, phenanthryl, 2- or 9-fluorenyl or anthracenyl, preferably C₆-C₁₂aryl such as phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl.

[0058] C₇-C₂₄aralkyl is typically benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω,ω-dimethyl-ω-phenyl-butyl, ω-phenyl-dodecyl, ω-phenyl-octadecyl, ω-phenyl-eicosyl or ω-phenyl-docosyl, preferably C₇-C₁₈aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, ω,ω-dimethyl-ω-phenyl-butyl, ω-phenyl-dodecyl or ω-phenyl-octadecyl, and particularly preferred C₇-C₁₂aralkyl such as benzyl, 2-benzyl-2-propyl, β-phenyl-ethyl, α,α-dimethylbenzyl, ω-phenyl-butyl, or ω,ω-dimethyl-ω-phenyl-butyl.

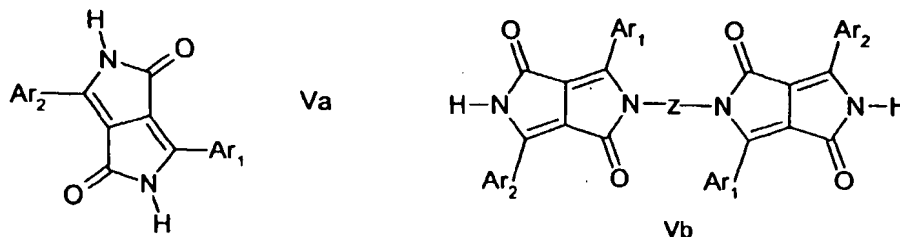
[0059] C₅-C₁₂cycloalkyl is typically cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, preferably cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl.

[0060] Heteroaryl with five to seven ring atoms, wherein nitrogen, oxygen or sulfur are the possible hetero atoms, is typically an unsaturated heterocyclic radical with five to 18 atoms having at least six conjugated π-electrons such as thienyl, benzo[b]thienyl, dibenzo[b,d]thienyl, thianthrenyl, furyl, furfuryl, 2H-pyranlyl, benzofuranyl, isobenzofuranyl, dibenzofuranyl, phenoxythienyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl, bipyridyl, triazinyl, pyrimidinyl, pyrazinyl, pyridazinyl, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, chinolyl, isochinolyl, phthalazinyl, naphthyridinyl, chinoxaliny, chinazoliny, cinnoliny, pteridinyl, carbazolyl, carboliny, benzotriazolyl, benzoxazolyl, phenanthridinyl, acridinyl, perimidinyl, phenanthroliny, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl or phenoxazinyl,

preferably the abovementioned mono- or bicyclic heterocyclic radicals.

[0061] The inventive DPP-compounds I can be synthesized according to methods well known in the art such as described in EP-A 133,156, e.g. in analogy to example 15.

[0062] A preferred embodiment of this invention relates to a process for the preparation of the inventive compounds I or III by treating in a first step the DPP derivative of formula Va or Vb



with a base, then, in a second step, treating the reaction mixture obtained in the first step with a usual alkylating agent, wherein in the first step the base is a hydride, an alkali metal alkoxide or a carbonate, and the alkylating agent is a sulfonate, tosylate, mesylate, carbonate, sulfate, or halogen compound of the formula $(R_1)_{1 \text{ or } 2}X$, wherein X stands for SO_3^- , $(p\text{-Me-phenyl})SO_2^-$, $(2,4,6\text{-trimethyl-phenyl})SO_2^-$, $-CO_3^-$, $-SO_4^-$, or halogen such as chlorine, bromine or iodine, preferably chlorine, bromine or iodine, particularly preferred for bromine or iodine, or a mixture of $(R_1)_{1 \text{ or } 2}X$ and $(R_2)_{1 \text{ or } 2}X$.

[0063] As a hydride usually an alkali metal hydride such as sodium hydride, lithium hydride, or potassium hydride, as an alkali metal alkoxide in general an alkali metal C_1 - C_4 alkoxide such as sodium or potassium tert. butoxide, sodium tert.-amylate, and as a carbonate usually sodium or potassium carbonate can be used, preferably sodium hydride.

[0064] Usually, the first step of the preferred preparation of compound I or III starting from compound Va, resp. Vb, is carried out at a temperature in the range of from -25 to 100, preferably from 0 to 25°C.

[0065] Preferably, the reaction is carried out in the presence of a solvent, preferably a dipolar aprotic solvent such as carboxamides, lactams, urea derivatives, sulfones and nitrobenzene such as dimethyl formamide ("DMF"), dimethyl acetamide ("DMA"), N-methylpyrrolidone ("NMP"), N,N'-dimethylethylene urea and N,N'-dimethylpropylene urea.

[0066] In case a solvent is used, a weight ratio of solvent to DPP-compound is chosen in the range of from 100:1 to 5:1, preferably from 25:1 to 10:1.

[0067] In addition, it is preferred to carry out the first step in the presence of a phase transfer catalyst such as a tetra alkyl ammonium halide such as tetraethyl ammonium bromide.

[0068] Usually, a molar ratio of base to DPP-compound Va, resp. Vb, is chosen in the range of from 10:1 to 2:1, preferably from 4:1 to 2:1.

[0069] Preferably, a molar ratio of DPP-compound Va, resp. Vb, to the phase transfer catalyst is chosen in the range of from 100:1 to 5:1, preferably from 25:1 to 10:1.

[0070] Generally, the reaction time depends *inter alia* on the reactivity of the chosen reactants and the chosen temperature. As an example, if room temperature is chosen as reaction temperature, a reaction time is as a rule in the range of from 0.5 to 24 hours.

[0071] Preferably, the halogen compound R_1-X (or the aforementioned mixture) is added to the reaction mixture obtained in the first step in the same solvent used in the first step.

The reaction temperature in the second process step usually is chosen in the range of from 0 to 160, preferably from 25 to 110°C, depending on *inter alia* the desired reaction pressure and solvent used.

The reaction time generally is chosen in the range of from 0.5 to 120, preferably from 12 to 60 hours.

[0072] As a rule the molar ratio of R_1-X to DPP compound Va, resp. Vb, is chosen in the range of from 10:1 to 2:1, preferably from 4:1 to 2:1.

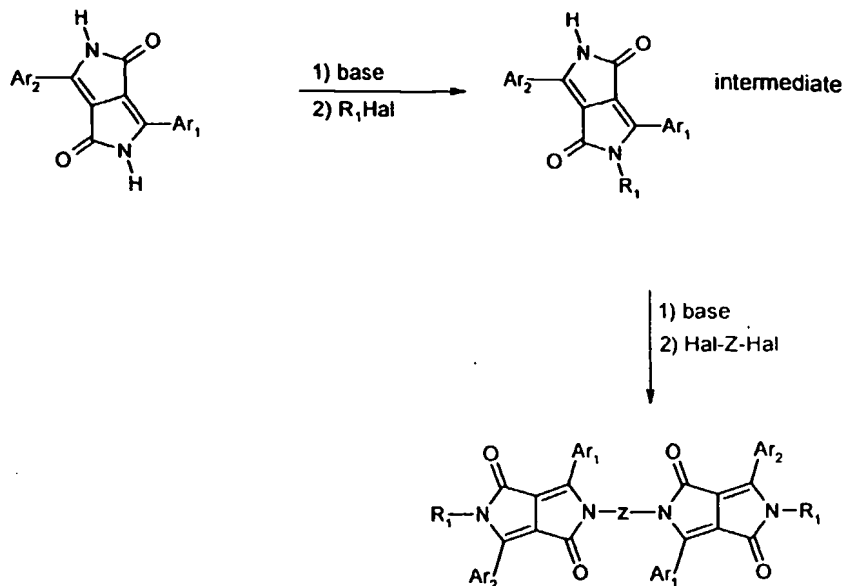
[0073] In case a solvent is used, the amount of solvent usually is chosen in the range of from 100:1 to 5:1, preferably from 25:1 to 10:1, based on the amount of halogen compound R_1-X . Further, preferably the same solvent is used as in the first step, if a solvent is used in the first step. If no solvent is used in the first step, the same solvents can be used as mentioned above.

[0074] The obtained reaction mixture can be worked up by applying methods well known in the art, e.g. by precipitating the product in the presence of an appropriate solvent such as water, and, if deemed necessary, by re-crystallization in an appropriate solvent such as ethanol. Other methods for example are the addition of an alcohol to quench the excess base followed by filtration.

[0075] Compounds Va are described e.g. in US 4,579,949, and/or can be prepared according to the method described therein, in which an appropriate nitrile is reacted with a corresponding dialkyl or diaryl succinate, e.g. $NC-Ar_1$ is reacted

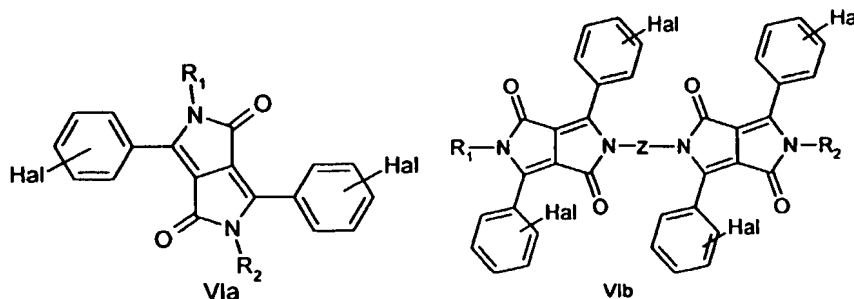
with sodium tert.-amyl alcohol followed by the addition of diisopropyl succinate. This method is preferred in case Ar_1 and/or Ar_2 stand for a biphenyl radical (i.e. R_5 and/or R_6 stand for phenyl or substituted phenyl in 4-position), or for the compounds described below (DPP VIa).

[0076] Compounds Vb can be prepared e.g. via the following route



Of course, instead of using R_1Hal , a mixture of R_1-Hal and R_2-Hal can be used which then would lead to the general formula Vb. Usually, R_1Hal , resp. the mixture of R_1Hal and R_2Hal , is used in a molar amount in the range of from 0.4-0.6:1, related to the starting DPP derivative. Accordingly, generally the molar amount of $Hal-Z-Hal$ /intermediate is chosen in the range of from 0.4-0.6:1.

[0077] Compounds I, resp. III, are also available in analogy to the method described in EP-A 353,184, which comprises reacting a DPP-compound of formula VIa or VIb



wherein Hal stands for halogen such as fluorine, chlorine, bromine or iodine, preferably chlorine or bromine, with a nucleophilic agent such as a secondary amine, HNR_8R_9 , a thiol, HSR_8 , or $HS(O)_nR_8$, an alcohol, HOR_{10} , a diselenide, $R_8(O)_nSe-Se(O)_nR_8$, preferably in a molar ratio of DPP VIa, resp. VIb, :nucleophilic agent in the range of 1.2:1 to 0.8:1, or, if R_2 has the same meaning as R_1 in the range of from 1:2.5 to 1:1, in the presence of an anhydrous dipolar aprotic solvent, and of an anhydrous base in an amount in the range of from usually 0.1 to 15 moles per mole of the nucleophilic agent, at a temperature in the range of from usually 100 to 220°C and under a pressure generally in the range of from 100 to 300 kPa.

[0078] Examples of suitable anhydrous dipolar aprotic solvents are carboxamides, lactams, urea derivatives, sulfones and nitrobenzene such as DMF, DMA, NMP, N,N'-dimethylethylene urea and N,N'-dimethylpropylene urea.

[0079] Suitable anhydrous bases are e.g. anhydrous organic bases such as quinoline, or preferably, an excess of

the secondary amine used for the amination, the aforementioned carbonates such as sodium or potassium carbonate and alkali metal hydrides such as sodium hydride. In case a diselenide, $R_7(O)_n\text{Se-Se}(O)_nR_7$, is used, an alkali metal hydride, preferably sodium hydride, has to be used as a base.

[0080] The corresponding 1- and 2-naphthyl-derivatives can be prepared analogously.

[0081] DPP-compounds VIa and VIb are known and/or can be prepared e.g. according to the method described in US 4,579,949, which methods comprises reacting a dialkyl or diaryl succinate with a nitrile, e.g. dimethyl succinate can be reacted with p-chloro benzonitrile according to example 6 in US 4,579,949 to yield the corresponding DPP compound VIa, in which Hal stands for chlorine.

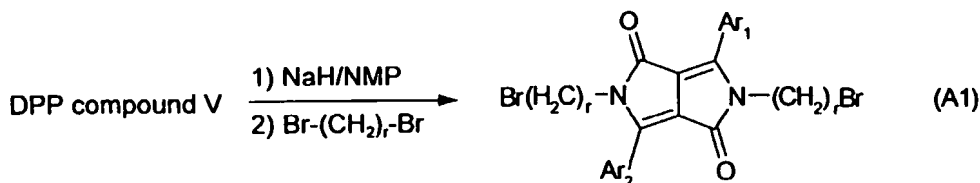
[0082] Compounds $R_1\text{-X}$ are commercially available or can be prepared by methods well known in the art.

[0083] A further embodiment of the invention on hand concerns a process for the preparation of the inventive compounds I resp. III

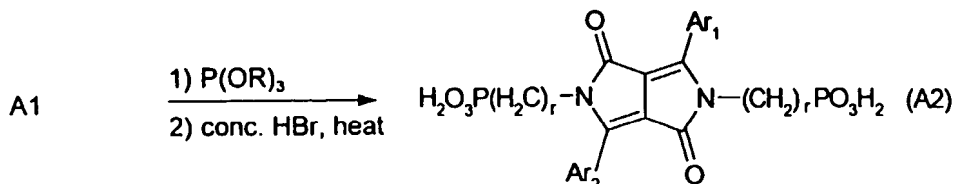
(a) in treating in a first step the DPP derivative of formula VIa, resp. VIb, with a nucleophilic agent such as a secondary amine, HNR_8R_9 , a thiol, HSR_8 , or $\text{HS}(\text{O})_n\text{R}_8$, an alcohol, HOR_{10} , a diselenide, $\text{R}_8(\text{O})_n\text{Se-Se}(\text{O})_n\text{R}_8$, preferably in a molar ratio of DPP VIa, resp. VIb, nucleophilic agent in the range of 1.2:1 to 0.8:1, or, if R_2 has the same meaning as R_1 in the range of from 1:2.5 to 1:1, in the presence of an anhydrous dipolar aprotic solvent, and of an anhydrous base in an amount in the range of from usually 0.1 to 15 moles per mole of the nucleophilic agent, at a temperature in the range of from usually 100 to 220°C and under a pressure generally in the range of from 100 to 300 kPa, and optionally isolating the obtained compound V,

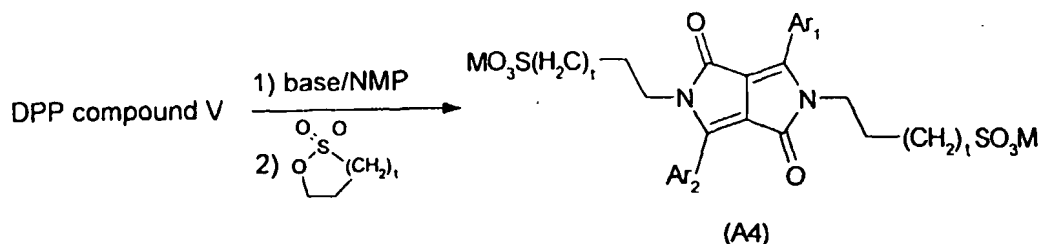
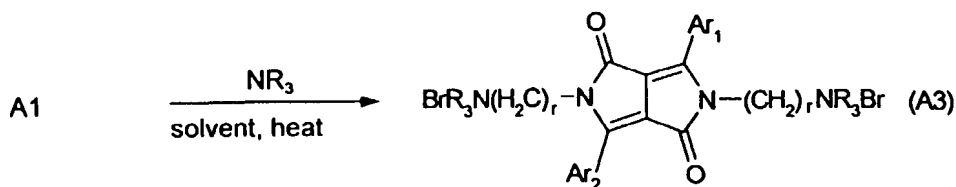
(b) then treating the obtained compound Va, resp. Vb, with a base, thereafter in a second step, treating the reaction mixture obtained in the first step of (b) with an usual alkylating agent, wherein in the first step of (b) the base is a hydride, an alkali metal alkoxide or a carbonate, and the alkylating agent is a sulfonate, tosylate, mesylate, carbonate, sulfate, or halogen compound of the formula $(\text{R}_1)_{1 \text{ or } 2}\text{X}$, wherein X stands for SO_3^- , (p-Me-phenyl) SO_2^- , (2,4,6-trimethyl-phenyl) SO_2^- , $-\text{CO}_3^-$, $-\text{SO}_4^-$, or halogen, or a mixture of $(\text{R}_1)_{1 \text{ or } 2}\text{X}$ and $(\text{R}_2)_{1 \text{ or } 2}\text{X}$ (it is evident, that the number of R_1 -units (either one or two) in $(\text{R}_1)_{1 \text{ or } 2}\text{X}$ depends on the nature of the chosen rest X, i.e. there can be only two R_1 -units if X stands for a divalent anion such as $-\text{CO}_3^-$, $-\text{SO}_4^-$ etc.).

[0084] Water-soluble compounds I, resp. III, i.e. inventive compounds I or III being substituted with a functional group capable of increasing the solubility in water such as a tertiary amino group, SO_3^- , or PO_4^{2-} , can be prepared by using well-known methods in the art. The following routes are representative examples, and, hence, do not restrict the invention just to these examples:



wherein r stands for an integer from usually 2 to 25; instead of linear alkyl groups, one could also use branched alkyl groups or aralkyl groups such as $\text{Br}-(\text{CH}_2)_{r1}\text{-aryl}-(\text{CH}_2)_{r2}\text{-Br}$, r_1 and r_2 usually being whole numbers in the range of from 0 to 10;





20 wherein M stands for a metal ion such as sodium
or potassium, and t is 1 or 2

25 [0085] Accordingly, corresponding compounds III are available via such route.

[0086] Another embodiment of the present invention is related to a method of coloring high molecular weight organic materials (having a molecular weight usually in the range of from 10^3 to 10^7 g/mol) by incorporating the inventive fluorescent DPP compounds I or III by known methods in the art.

[0087] As high molecular weight organic materials the following can be used such as biopolymers, and plastic materials, including fibres.

30 [0088] The present invention relates preferably to the use of the inventive DPPs I or III for the preparation of

inks, for printing inks in printing processes, for flexographic printing, screen printing, packaging printing, security ink printing, intaglio printing or offset printing, for pre-press stages and for textile printing, for office, home applications or graphics applications, such as for paper goods, for example, for ballpoint pens, felt tips, fiber tips, card, wood, (wood) stains, metal, inking pads or inks for impact printing processes (with impact-pressure ink ribbons), for the preparation of

35 colorants, for coating materials, for industrial or commercial use, for textile decoration and industrial marking, for roller coatings or powder coatings or for automotive finishes, for high-solids (low-solvent), water-containing or metallic coating materials or for pigmented formulations for aqueous paints, for the preparation of pigmented plastics for coatings, fibers, platters or mold carriers, for the preparation of non-impact-printing material for digital printing, for the thermal wax transfer printing process, the ink jet printing process or for the thermal transfer printing process, and also for the preparation of color filters, especially for visible light in the range from 400 to 700 nm, for liquid-crystal displays (LCDs) or charge combined devices (CCDs) or for the preparation of cosmetics or for the preparation of

40 polymeric ink particles, toners, dry copy toners liquid copy toners, or electrophotographic toners.

45 [0089] Illustrative examples of suitable organic materials of high molecular weight which can be colored with the inventive fluorescent DPPs I or III of this invention are vinyl polymers, for example polystyrene, poly- α -methylstyrene, poly-p-methylstyrene, poly-p-hydroxystyrene, poly-p-hydroxyphenylstyrene, polymethyl methacrylate and polyacrylamide as well as the corresponding methacrylic compounds, polymethylmaleate, polyacrylonitrile, polymethacrylonitrile, polyvinyl chloride, polyvinyl fluoride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl acetate, polymethyl vinyl ether and polybutyl vinyl ether; polymers which are derived from maleinimide and/or maleic anhydride, such as copolymers of maleic anhydride with styrene; polyvinyl pyrrolidone; ABS; ASA; polyamides; polyimides; polyamidimides; polysulfones; polyether sulfones; polyphenylene oxides; polyurethanes; polyureas; polycarbonates; polyarylenes; polyarylene sulfides; polyepoxides; polyolefins such as polyethylene and polypropylene; polyalkadienes; biopolymers and the derivatives thereof e.g. cellulose, cellulose ethers and esters such as ethylcellulose, nitrocellulose, cellulose acetate

50 55

and cellulose butyrate, starch, chitin, chitosan, gelatin, zein; natural resins; synthetic resins such as alkyd resins, acrylic resins, phenolic resins, epoxide resins, aminoformaldehyde resins such as urea/formaldehyde resins and melamine/formaldehyde resin; vulcanized rubber; casein; silicone and silicone resins; rubber, chlorinated rubber; and also polymers which are used, for example, as binders in paint systems, such as novolaks which are derived from C₁-C₆-aldehydes such as formaldehyde and acetaldehyde and a binuclear or mononuclear, preferably mononuclear, phenol which, if desired, is substituted by one or two C₁-C₉alkyl groups, one or two halogen atoms or one phenyl ring, such as o-, m- or p-cresol, xylene, p-tert.-butylphenol, o-, m- or p-nonylphenol, p-chlorophenol or p-phenylphenol, or a compound having more than one phenolic group such as resorcinol, bis(4-hydroxyphenyl)methane or 2,2-bis(4-hydroxyphenyl)propane; as well as suitable mixtures of said materials.

[0090] Particularly preferred high molecular weight organic materials, in particular for the preparation of a paint system, a printing ink or ink, are, for example, cellulose ethers and esters, e.g. ethylcellulose, nitrocellulose, cellulose acetate and cellulose butyrate, natural resins or synthetic resins (polymerization or condensation resins) such as aminoplasts, in particular urea/formaldehyde and melamine/formaldehyde resins, alkyd resins, phenolic plastics, polycarbonates, polyolefins, polystyrene, polyvinyl chloride, polyamides, polyurethanes, polyester, ABS, ASA, polyphenylene oxides, vulcanized rubber, casein, silicone and silicone resins as well as their possible mixtures with one another.

[0091] It is also possible to use high molecular weight organic materials in dissolved form as film formers, for example boiled linseed oil, nitrocellulose, alkyd resins, phenolic resins, melamine/formaldehyde and urea/formaldehyde resins as well as acrylic resins.

[0092] Said high molecular weight organic materials may be obtained singly or in admixture, for example in the form of granules, plastic materials, melts or in the form of solutions, in particular for the preparation of spinning solutions, paint systems, coating materials, inks or printing inks.

[0093] In a particularly preferred embodiment of this invention, the inventive fluorescent DPPs I or III are used for the mass coloration of polyvinyl chloride, polyamides and, especially, polyolefins such as polyethylene and polypropylene as well as for the preparation of paint systems, including powder coatings, inks, printing inks, color filters and coating colors.

[0094] Illustrative examples of preferred binders for paint systems are alkyd/melamine resin paints, acryl/melamine resin paints, cellulose acetate/cellulose butyrate paints and two-pack system lacquers based on acrylic resins which are crosslinkable with polyisocyanate.

[0095] According to observations made to date, the inventive fluorescent DPPs I or III can be added in any desired amount to the material to be colored, depending on the end use requirements. In the case of high molecular weight organic materials, for example, the fluorescent DPPs I or III prepared according to this invention can be used in an amount in the range from 0.01 to 40, preferably from 0.01 to 5% by weight, based on the total weight of the colored high molecular weight organic material.

[0096] Hence, another embodiment of the present invention relates to a composition comprising

- (a) 0.01 to 50, preferably 0.01 to 5, particularly preferred 0.01 to 2% by weight, based on the total weight of the colored high molecular organic material, of a fluorescent DPP I or III according to the present invention, and
- (b) 99.99 to 50, preferably 99.99 to 95, particularly preferred 99.99 to 98% by weight, based on the total weight of the colored high molecular organic material, of a high molecular organic material, and
- (c) if desired, customary additives such as rheology improvers, dispersants, fillers, paint auxiliaries, siccatives, plasticizers, UV-stabilizers, and/or additional pigments or corresponding precursors in effective amounts, such as e.g. from 0 to 50% by weight, based on the total weight of (a) and (b).

[0097] To produce non-brittle mouldings or to diminish their brittleness, so-called plasticizers can be added to the high molecular weight organic materials prior to moulding. Plasticizers may be, for example, esters of phosphoric acid, phthalic acid and sebacic acid. Said plasticizers may be added before, during or after pigmenting the high molecular weight organic materials with the inventive fluorescent DPPs I or III.

[0098] To obtain different shades, the inventive fluorescent DPPs I or III may advantageously be used in admixture with fillers, transparent and opaque white, colored and/or black pigments as well as customary luster pigments in the desired amount.

[0099] For the preparation of paint systems, coating materials, color filters, inks and printing inks, the corresponding high molecular weight organic materials, such as binders, synthetic resin dispersions etc. and the inventive fluorescent DPPs I or III are usually dispersed or dissolved together, if desired together with customary additives such as dispersants, fillers, paint auxiliaries, siccatives, plasticizers and/or additional pigments or pigment precursors, in a common solvent or mixture of solvents. This can be achieved by dispersing or dissolving the individual components by themselves, or also several components together, and only then bringing all components together, or by adding everything together at once.

[0100] Hence, a further embodiment of the present invention relates to a method of using the inventive fluorescent

DPPs I or III for the preparation of dispersions and the corresponding dispersions, and paint systems, coating materials, color filters, inks and printing inks comprising the inventive fluorescent DPPs I or III.

[0101] A particularly preferred embodiment relates to the use of the inventive DPPs I or III for the preparation of fluorescent tracers for e.g. leak detection of fluids such as lubricants, cooling systems etc., as well as to fluorescent tracers or lubricants comprising the inventive DPPs I or III. Usually, such lubricant compositions, e.g. for a refrigerant, comprise an oil selected from the group consisting of naphthalenic oils, paraffinic oils, alkylated benzene oils, polyalkyl silicate oils, polyglycols, esters, polyether polyols, polyvinyl ethers, polycarbonates, fluorinated silicones, perfluoroethers, aromatic compounds with fluoroalkyloxy or fluoroalkylthio substituents. The amount of the inventive DPP I or III in the lubricant is chosen generally in an amount of from 100 to 1000 ppm. If the inventive compound I is water-soluble, it could be used as tracer in water as well.

[0102] A particular embodiment of this invention concerns ink jet inks comprising the inventive fluorescent compositions

[0103] The desired ink may contain up to 30 % by weight of the fluorescent composition, but will generally be in the range of 0.1 to 10, preferably from 0.1 to 8% by weight of the total ink composition for most thermal ink jet printing applications.

[0104] Further, the inks usually contain polymeric dispersants such as random, block, branched or graft polymers or copolymers. Most preferred are polymeric dispersants made by the group transfer polymerization process, because in general these are free from higher molecular weight species that tend to plug pen nozzles.

[0105] In AB or BAB block copolymers, the A segment usually is a hydrophobic homopolymer or copolymer which serves to link with the inventive fluorescent composition and the B block generally is a hydrophilic homopolymer or copolymer, or salts thereof and serves to disperse the pigment in the preferably chosen aqueous medium. Such polymeric dispersants and the synthesis thereof are known from e.g. US 5,085,698.

[0106] ABC triblocks are also useful as dispersants. In the ABC triblock, the A block usually is a polymer compatible with water, the B block is a polymer capable of binding to the fluorescent composition and the C block is compatible with the organic solvent. Preferably the A and C blocks are end blocks. ABC triblocks and their synthesis are disclosed e.g. in EP-A 556,649. Suitable graft polymers are disclosed in US 5,231,131.

[0107] Representative compounds useful for this purpose include e.g. polymers of polyvinyl alcohol, cellulose and ethylene oxide modified polymers, and dispersant compounds containing ionisable groups such as acrylic acid, maleic acid or sulfonic acid.

[0108] The polymeric dispersant is generally present in an amount in the range of from 0.1 to 30, preferably from 0.1 to 8% by weight of the total ink composition.

[0109] In addition to, or in place of the preferred polymeric dispersants, surfactants may be used as dispersants. These may be anionic, nonionic, or amphoteric surfactants. A detailed list of non-polymeric as well as some polymeric dispersants is disclosed in the section on dispersants of Manufacturing Confection Publishing Co., (1990) p. 110-129, McCutcheon's Functional Materials, North America Edition.

[0110] Usually the ink contains an aqueous medium such as water or a mixture of water and at least one water-soluble organic solvent. Water-soluble organic solvents are well known, representative examples of which are disclosed in e.g. US 5,085,698. Selection of a suitable mixture of water and water-soluble organic solvent depends on usually requirements of the specific application such as desired surface tension and viscosity, drying time of the ink, and the media substrate onto which the ink will be printed.

[0111] Particularly preferred is a mixture of a water-soluble solvent having at least two hydroxyl groups, e.g. diethylene glycol, and water, especially deionized water.

[0112] In the event that a mixture of water and a water-soluble organic solvent is used as aqueous medium, water usually would comprise from 30 to 95, preferably 60 to 95% by weight, based on the total weight of the aqueous medium.

[0113] The amount of aqueous medium generally is in the range of from 70 to 99.8, preferably from 84 to 99.8%, based on the total weight of the ink.

[0114] The ink may contain other ingredients well known to those skilled in the art such as surfactants to alter surface tension as well as to maximize penetration. However, because surfactants may destabilize dispersions, care should be taken to insure compatibility of the surfactant with the other ink components. In general, in aqueous inks, the surfactants may be present in amounts ranging from 0.01 to 5, preferably from 0.2 to 3% by weight, based on the total weight of the ink.

[0115] Biocides may be used in the ink compositions to inhibit growth of microorganisms. Sequestering agents such as EDTA may also be included to eliminate deleterious effects of heavy metal impurities. Other known additives, such as viscosity modifiers may also be added.

[0116] A further embodiment concerns the use of the inventive fluorescent compounds I in phase change ink jet inks. The preparation of such inks is well known in the art, e.g. described in detail in EP-A 816, 410.

[0117] For the pigmentation of high molecular weight organic material, the inventive DPPs I or III, optionally in the form of masterbatches, usually are mixed with the high molecular weight organic materials using roll mills, mixing

apparatus or grinding apparatus. Generally, the pigmented material is subsequently brought into the desired final form by conventional processes, such as calendering, compression molding, extrusion, spreading, casting or injection molding. In order to prepare non-rigid moldings or to reduce their brittleness it is often desired to incorporate so-called plasticizers into the high molecular weight organic materials prior to forming. Examples of compounds which can be used as such plasticizers are esters of phosphoric acid, phthalic acid or sebacic acid. The plasticizers can be added before or after the incorporation of the inventive DPPs I or III into the polymers. It is also possible, in order to achieve different hues, to add fillers or other coloring constituents such as white, color or black pigments in desired amounts to the high molecular weight organic materials in addition to the inventive DPPs I or III.

[0118] For pigmenting lacquers, coating materials and printing inks the high molecular weight organic materials and the inventive DPPs I or III, alone or together with additives, such as fillers, other pigments, siccatives or plasticizers, are generally dissolved or dispersed in a common organic solvent or solvent mixture. In this case it is possible to adopt a procedure whereby the individual components are dispersed or dissolved individually or else two or more are dispersed or dissolved together and only then are all of the components combined.

[0119] The present invention additionally relates to inks comprising a coloristically effective amount of the pigment dispersion of the inventive DPPs I or III.

[0120] Processes for producing inks especially for ink jet printing are generally known and are described for example in US 5,106,412.

[0121] The inks can be prepared, for example, by mixing the pigment dispersions comprising the inventive DPPs I or III with polymeric dispersants.

[0122] The mixing of the pigment dispersions with the polymeric dispersant takes place preferably in accordance with generally known methods of mixing, such as stirring or mechanical mixing; it is preferably advisable to use intensive mechanical mixers such as the so-called ULTRATURAX® stirrer from Kunkel & Jahn, Staufen (Germany).

[0123] When mixing a DPP I or III with polymeric dispersants it is preferred to use a water-dilutable organic solvent.

[0124] The weight ratio of the pigment dispersion to the ink in general is chosen in the range of from 0.001 to 75% by weight, preferably from 0.01 to 50% by weight, based on the overall weight of the ink.

[0125] Examples of suitable polymeric dispersants are carboxyl-containing polyacrylic resins such as polymeric methacrylic or crotonic acids, especially those obtained by addition polymerization of acrylic acid or acrylic acid and other acrylic monomers such as acrylates.

[0126] Depending on the field of use or when using DPP I or III, it is also possible, if desired, to admix a small proportion of a water-miscible organic solvent in from 0.01 to 30% by weight, based on the overall weight of the ink, and/or to admix water and/or bases so as to give a pH in the range from 7 to 11. It may likewise be advantageous to add preservatives, antifoams, surfactants, light stabilizers and pH regulators, for example, to the ink of the invention, depending on the field of use.

[0127] Examples of suitable pH regulators are inorganic salts such as lithium hydroxide or lithium carbonate, quaternary ammonium hydroxide or ammonium carbonate. Examples of preservatives and antifoams are, for example, sodium dehydroacetate, 2,2-dimethyl-6-acetoxydioxane or ammonium thioglycolate. It is also possible to employ known agents which regulate the viscosity or the surface tension and are described in e.g. US 5,085,698.

[0128] Examples of water-miscible organic solvents are aliphatic C₁-C₄alcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, tert.-butanol, ketones such as acetone methyl ethyl ketone, methyl isobutyl ketone or diacetone alcohol, and also polyols, Cellosolves® and carbitols, such as ethylene glycol, diethylene glycol, triethylene glycol, glycerol, propylene glycol, ethylene glycol monomethyl or monoethyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, ethylene glycol phenyl ether, propylene glycol phenyl ether, diethylene glycol monomethyl or monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl or monoethyl ether, and also N-methyl-2-pyrrolidone, 2-pyrrolidone, N,N'-dimethylformamide or N,N'-dimethylacetamide.

[0129] If desired, the ink prepared as described above can be worked up further. The working up of the ink can be carried out by the customary methods for working up dispersions, by separation techniques, such as sieving or centrifuging the coarse particles from the resulting dispersion. It has been found advantageous, too, to carry out centrifuging in two stages of different intensity, e.g. centrifuging in a first step for from ten minutes to one hour at from 2000 to 4000 rpm and then, in a second step, for from 10 minutes to one hour at from 6000 to 10000 rpm.

[0130] Following centrifuging or sieving, the dispersion usually can be used directly as an ink for ink jet printing, for example.

[0131] The present invention additionally relates to a process for producing color filters comprising a transparent substrate and applied thereon a red, blue and green layer in any desired sequence, by using a red compound I and known blue and green compounds. The different colored layers preferably exhibit patterns such that over at least 5% of their respective surface they do not overlap and with very particular preference do not overlap at all.

[0132] The preparation and use of color filters or color-pigmented high molecular weight organic materials are well-known in the art and described e.g. in Displays 14/2, 1151 (1993), EP-A 784085, or GB-A 2,310,072.

[0133] The color filters can be coated for example using inks, especially printing inks, which can comprise pigment

dispersions comprising the inventive DPPs I or III or can be prepared for example by mixing a pigment dispersion comprising a DPP I or III with chemically, thermally or photolytically structurable high molecular weight organic material (so-called resist). The subsequent preparation can be carried out, for example, in analogy to EP-A 654 711 by application to a substrate, such as a LCD, subsequent photostructuring and development.

[0134] Particular preference for the production of color filters is given to pigment dispersions comprising a DPP I or III which possess non-aqueous solvents or dispersion media for polymers.

[0135] The present invention relates, moreover, to toners comprising a pigment dispersion containing a DPP I or III or a high molecular weight organic material pigmented with a DPP I or III in a coloristically effective amount.

[0136] In a particular embodiment of the process of the invention, toners, coating materials, inks or colored plastics are prepared by processing masterbatches of toners, coating materials, inks or colored plastics in roll mills, mixing apparatus or grinding apparatus.

[0137] The present invention additionally relates to colorants, colored plastics, polymeric ink particles, or non-impact-printing material comprising an inventive DPP I or III pigment, preferably in the form of a dispersion, or a high molecular weight organic material pigmented with a DPP I or III in a coloristically effective amount.

[0138] A coloristically effective amount of the pigment dispersion according to this invention comprising an inventive DPP I or III denotes in general from 0.0001 to 99.99% by weight, preferably from 0.001 to 50% by weight and, with particular preference, from 0.01 to 50% by weight, based on the overall weight of the material pigmented therewith.

[0139] Further, the inventive compounds I can be used for textile application and for the dying of paper.

[0140] Another preferred embodiment concerns to the use of the inventive compounds for color changing media.

There are three major techniques in order to realize full-color organic electroluminescent devices:

(i) to use the three primary colors blue, red and green by electroluminescence,

(ii) to convert electroluminescent blue to photoluminescent green and red via color changing media which absorb the above electroluminescent blue and fluoresce in green and red,

(iii) to convert white electroluminescent emission to blue, green and red via classical color filters.

[0141] The inventive compounds are useful for EL materials for the above category (i). In addition, the inventive compounds are also useful for the above technique (ii). This is because the invented compounds can exhibit strong photoluminescence as well as electroluminescence.

[0142] Technique (ii) is known for example from US 5,126,214 in which a method is described wherein EL blue with a maximum wavelength of ca. 480 nm to green, yellowish green, orange and red using coumarin, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran, pyridine, rhodamine 6G, phenoxazone and other dyes.

[0143] In contrast to known red fluorescent dyes (thioindigos) the inventive DPPs I or III can be applied to color polyamides, because they do not decompose during the incorporation into the polyamides. Further, they exhibit an exceptionally good lightfastness, a superior heat stability, especially in plastics.

Examples

[0144] The solid state absorbance spectra are measured on a Perkin-Elmer Lambda 9 UV/VIS-spectrometer and the solid state fluorescence spectra on a Perkin-Elmer MPF 66 with a 5cm Ulbricht-sphere. The measurements are carried out with flexible PVC containing 0.02% by weight of the inventive compounds.

Example 1:

[0145] Sodium hydride (60% dispersion in mineral oil, 47 g, 1.175 mol) is added portionwise over a 30-minutes period without external cooling and under nitrogen to a slurry of 1,4-diketo-3,6-bis-(4'-t-butylphenyl)pyrrolo[3,4-c]pyrrole (140 g, 0.33 mol) in 1-methyl-2-pyrrolidone (2 liters). After two hours the reaction mixture is cooled in an ice-water bath for 30 minutes, then benzyl bromide (216 g, 1.263 mol) is added dropwise (over 30 minutes). The reaction mixture is then slowly warmed-up to room temperature (by keeping the reaction flask in the cooling bath and allowing the ice in the bath to melt) and stirred at this temperature for 10 hours. Then acetic acid (50 ml), water (50 ml) and acetone (1.5 liters) are successively added. After stirring for 1 hour, a red solid is filtered off, washed with acetone (500 ml), water (4 liters), ethanol (1 liter), hexane (1 liter) and acetone (500 ml) and then dried under a reduced atmosphere at 50°C for 24 hours. Yield: 104 g (53%) of bright red solid 1,4-diketo-2,5-dibenzyl-3,6-bis-(4'-t-butylphenyl)pyrrolo[3,4-c]pyrrole.

Example 2:

[0146] Example 1 is repeated except that 1,4-diketo-3,6-bis-(4'-chlorophenyl)pyrrolo-[3,4-c]pyrrole is used and then

1,4-diketo-2,5-dibenzyl-3,6-di-(4'-chloro-phenyl)pyrrolo[3,4-c]pyrrole is obtained. Yield: 58%

Example 3:

[0147] Sodium hydride (60% by weight in mineral oil, 3.84 g, 0.088 mol) is added portionwise to di-(4-chlorophenyl) diselenide (16.76 g, 0.044 mol) in DMF (200 ml) at room temperature under an atmosphere of nitrogen. The reaction mixture is then heated in an oil bath at 70°C for one hour, then 1,4-diketo-2,5-dibenzyl-3,6-di-(4'-chloro-phenyl)pyrrolo [3,4-c]pyrrole (obtained according to example 2) (21.5 g, 0.040 mol) is added and the reaction mixture is heated to 140°C for five hours. After cooling to room temperature, water (500 ml) is added and the reaction mixture is heated to 100°C for 30 min. The obtained solid is filtered off, washed with water, then ethanol, and finally dried under an atmosphere of reduced pressure at a temperature of 50°C for 24 hours. Yield: 96% (32.44 g, 0.038 mol) of dark red solid 1,4-diketo-2,5-dibenzyl-3,6-di-(4'-(4"-chlorophenyl)selenenyl)phenyl) pyrrolo[3,4-c]pyrrole with a melting point in the range of from 248 to 250°C.

Example 4:

[0148] Example 1 is repeated except that n-butyl iodide is used as alkylating agent. Yield: 33%.

Example 5:

[0149] Example 4 is repeated except that 1,4-diketo-3,6-bis-(4'-methylphenyl)pyrrolo-[3,4-c]pyrrole used Yield: 54%.

Example 6:

[0150] Example 5 is repeated except that 1,4-diketo-3,6-bis-(4'-biphenyl)pyrrolo[3,4-c]pyrrole is used. Yield: 58%.

Example 7:

[0151] Example 6 is repeated except that 2-naphthylmethyl bromide is used as alkylating agent. Yield: 51%.

Example 8:

[0152] Example 1 is repeated except that 1,4-diketo-3,6-bis-(4-(4-morpholinyl)phenyl)pyrrolo[3,4-c]pyrrol (obtained according to example 4 of EP-A 353,184) is used. Yield: 64%.

Example 9:

[0153] Example 7 is repeated except that 1,4-diketo-3,6-bis-(4-(4-morpholinyl)phenyl)pyrrolo[3,4-c]pyrrol is used. Yield: 19%.

Example 10:

[0154]

(a) Triphenyl amine (98.32 g, 0.393 mol) is suspended in DMF (280 ml). Phosphorus oxychloride (66.24 g, 0.432 mol) is added dropwise to it over a 30-minutes period without external cooling. After stirring for one more hour, the reaction is heated to 80°C (bath temperature) for 2 ½ hours. After cooling to room temperature, the reaction is slowly poured onto ice-cold water (8 liters) with vigorous stirring. After 30 minutes, aqueous sodium hydroxide (5 N, 250 ml) is added to the reaction, and stirring is continued for one hour. The obtained precipitate is filtered off, washed with water (2 liters), then with methanol (2 litres) and dried to give 4-diphenylaminobenzaldehyde as a beige solid (90.47 g, 0.331 mol, 84 %), which is used in the next step without further purification.

(b) 48.7 g of the above obtained 4-diphenylaminobenzaldehyde (0.178 mol) is suspended in formic acid (400 ml). Hydroxylamine sulfate is added (16.08 g, 0.098 mol), followed by sodium formate (14.15 g, 0.214 mol). The reaction is heated under reflux for 3 hours. Then the solvent is removed under vacuum. The residue is suspended in toluene (800 ml). The residual solid is filtered off and discarded. Solvents are evaporated and the residue is dissolved in a minimum amount of dichloromethane. This solution is filtered through a pad of silica gel, using dichloromethane as solvent. The solvent is then evaporated under vacuum. The thus obtained solid is taken up in toluene (350 ml)

and heated to reflux in the presence of charcoal. After filtering hot, the solvent is removed from the filtrate to give 4-diphenylaminobenzonitrile (42.01 g, 0.155 mol, 87%) as a beige solid, which is taken to the next step without further purification.

(c) Sodium pieces (24.5 g, 1.064 mol) are added to tert.-amyl alcohol (400 ml). Then 20 mg of anhydrous FeCl_3 are added. The reaction mixture is slowly heated until a gentle reflux is obtained. After two hours, all sodium is reacted. 134.54 g of the above obtained 4-diphenylaminobenzonitrile (0.501 mol) are added in portions over a period of 15 minutes. Then di-tert.-butyl succinate (79.5 g, 0.346 mol) in tert.-amyl alcohol (300 ml) is added over 1.75 hours. After an additional hour of heating to reflux, the reaction mixture is cooled to room temperature and stirred overnight. Then, the reaction mixture is slowly added into a mixture of water (1200 ml) and methanol (600 ml) and stirred for 3 hours. The thus obtained solid is then filtered, washed with first water and then ethanol, and afterwards dried at 50°C overnight. 70.96 g (0.114 mol, 46%) of 1,4-diketo-3,6-bis-(4-diphenylaminophenyl)pyrrolo [3,4-c]pyrrole are obtained as a violet powder. $^1\text{H-NMR}$ (300 MHz, $\text{d}^6\text{-DMSO}$): 6.91 (d, 4 H, $J = 9$ Hz); 7.15-7.22 (m, 12 H); 7.38-7.43 (m, 8 H); 8.32 (d, 4 H, $J = 9$ Hz); 11.02 (broad s, 2 H).

(d) Example 1 is repeated except that the above obtained 1,4-diketo-3,6-bis-(4-diphenylaminophenyl)pyrrolo[3,4-c]pyrrol is used. Yield: 56%.

Example 11:

[0155] 1.02 g (2.3 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole is slurred in 15 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 0.35 g of sodium hydride (60-72% dispersion in mineral oil) is added to the slurry under nitrogen. After stirring for 2 hours, 1.62 g (6.6 mmol) of 2-phenylbenzyl bromide is added to the reaction mixture and then the mixture is stirred additionally for 2 hours. The mixture was poured into 50 ml of water and the red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After dried, 0.327 g (18%) of a red solid is obtained.

Example 12:

[0156] Example 11 is repeated except that 4-tert-butylbenzyl bromide is used as alkylating agent. Red solid (Yield: 63%).

Example 13:

[0157] 2.09 g (4.75 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 30 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 1.29 g (11.52 mmol) of potassium tert.-butoxide are added to the slurry under nitrogen. After stirring for 2 hours, 2.05 g (11.1 mmol) of 3-methylbenzyl bromide are added to the reaction mixture and then the mixture is stirred additionally for 2 hours. The mixture is poured into 50 ml of water and the red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 1.89 g (61%) of a red solid are obtained.

Example 14:

[0158] example 11 is repeated except that 1,4-diketo--3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Red solid (Yield 18%).

Example 15:

[0159] example 14 is repeated except that 4-tert-butylbenzyl bromide is used as alkylating agent. Red solid (Yield: 13%).

Example 16:

[0160] Example 14 is repeated except that 2-methylbenzyl bromide is used as alkylating agent. Red solid (Yield: 27%).

Example 17:

[0161] Example 14 is repeated except that 3-methylbenzyl bromide is used as alkylating agent. Red solid (Yield: 9.3%).

Example 18:

[0162] Example 13 is repeated except that 3,5-dimethylbenzyl bromide is used as alkylating agent. Red solid (Yield: 24%).

Example 19:

[0163] Example 14 is repeated except that 3,5-dimethylbenzyl bromide is used as alkylating agent. Red solid (Yield: 54%).

Example 20:

[0164] Example 13 is repeated except that 4-methyl benzylbromide is used as alkylating agent. Red solid (Yield: 62%).

Example 21:

[0165] example 14 is repeated except that 4-methylbenzyl bromide is used as alkylating agent. Red solid (Yield: 57%).

Example 22:

[0166] 24.6 g of potassium tert.-butoxide, 30 g of 2-naphthonitrile and 200 ml of tert.-amyl alcohol are heated up to 100°C under a nitrogen atmosphere. As soon as the this temperature has been reached, a solution of 23 g of di-n-butyl succinate and 70 ml of tert.-amyl alcohol is added over 1 hour using a dropping funnel. When the addition is completed, the reaction mixture is kept for 16 hours at 100°C, then cooled to 65°C, neutralized with 20 ml of glacial acetic acid and boiled briefly to reflux. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 300 ml of methanol and the pigment is isolated again by filtration, then finally washed with methanol and water until washings run colourless, and dried at 100°C in an atmosphere under reduced pressure affording 26.1 g (69% of theory, based on dibutyl succinate) of pure pigment of 1,4-diketo-3,6-bis-(2-naphthyl)-pyrrolo-(3,4-c)-pyrrole.

[0167] And then, Example 18 is repeated except that 1,4-diketo-3,6-bis-(2-naphthyl)-pyrrolo-(3,4-c)pyrrole is used as starting material. Red solid (Yield: 36%).

Example 23:

[0168] Example 22 is repeated except that benzyl bromide is used as alkylating agent. Orange solid (Yield: 30 %).

Example 24:

[0169] Example 22 is repeated except that 2-methylbenzyl bromide is used as alkylating agent. Orange solid (Yield: 30 %).

Example 25:

[0170] Example 22 is repeated except that 2-phenylbenzyl bromide is used as alkylating agent. Red solid (Yield: 8 %).

Example 26:

[0171] Example 13 is repeated except that 4-phenylbenzyl bromide is used as alkylating agent. Red solid (Yield: 50%).

Example 27:

[0172] 2.0 g (4.54 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 30 ml of 1-methyl-

2-pyrrolidinone for 2 hours at room temperature. 1.3 g (11.61 mmol) of potassium tert.-butoxide are added to the slurry under nitrogen. After stirring for 2 hours, 2.07 g (11.2 mmol) of 2-methylbenzyl bromide are added to the reaction mixture and then the mixture is stirred additionally for 2 hours. The mixture is poured into 50 ml of water and the red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 0.866 g (29%) of a red solid are obtained.

Example 28:

[0173] Example 27 is repeated except that 3-phenylbenzyl bromide is used as alkylating agent. Red solid (Yield: 38%).

Example 29:

[0174] Example 22 is repeated except that 3-methylbenzyl bromide and 1,4-diketo-3,6-bis-(2-naphthyl)-pyrrolo-(3,4-c)-pyrrole are used as alkylating agent and starting material, respectively. Red solid (Yield: 30%).

Example 30:

[0175] And then, Example 29 is repeated except that 4-methylbenzyl bromide is used as alkylating agent. Red solid (Yield: 36%).

Example 31:

[0176] Example 29 is repeated except that 4-phenylbenzyl bromide is used as alkylating agent. Orange solid (Yield: 30 %).

Example 32:

[0177] Example 31 is repeated except that 1,4-diketo-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Red solid (Yield: 30%).

Example 33:

[0178] Example 27 is repeated except that 1-bromoethyl benzene is used as alkylating agent. Yellow solid (Yield: 11.4%).

Example 34:

[0179] Example 33 is repeated except that 1,4-diketo-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Yellow solid (Yield: 35%).

Example 35:

[0180] 9.2 g of potassium tert.-butoxide, 15 g of 6-methoxy-2-naphthonitrile and 80 ml of tert.-amyl alcohol are heated up to 100°C under a nitrogen atmosphere. As soon as the this temperature is reached, a solution of 9.4 g of di-n-butyl succinate and 20 ml of tert.-amyl alcohol is added over 1 hour using a dropping funnel. When the addition is completed, the reaction mixture is kept for 12 hours at 100°C, then cooled to 65°C, neutralized with 20 ml of glacial acetic acid and boiled briefly to reflux. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 300 ml of methanol and the pigment is isolated again by filtration, then finally washed with methanol and water until washings run colourless, and dried at 100°C in an atmosphere under reduced pressure which affords 4.2 g (23% of theory, based on dibutyl succinate) of 1,4-diketo-3,6-bis-(2-(6-methoxynaphthyl))-pyrrolo-(3,4-c)-pyrrole. Example 29 is repeated except that 1,4-diketo-3,6-bis-(6-methoxy-2-naphthyl)-pyrrolo-(3,4-c)-pyrrole are used as starting material. Yellow solid (Yield: 21%).

Example 36:

[0181] Example 35 is repeated except that 3,5-dimethylbenzyl bromide is used as alkylating agent. Yellow solid (Yield: 38%).

Example 37:

[0182] 2.2 g (5.0 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 20 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 1.4 g (13.0 mmol) of potassium t-butoxide are added to the slurry under nitrogen. After stirring for 2 hours, 2.78 g (12 mmol) of (2-iodoethyl) benzene are added to the reaction mixture. The mixture is heated up to 80°C and stirred additionally for 3 hours. After cooling to room temperature, the mixture is poured into 50 ml of water and a red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 0.16 g (5%) of a red solid are obtained.

Example 38:

[0183] Example 37 is repeated except that 1,4-diketo-3,6-bis-(2-naphthyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material (Yield: 29%).

Example 39:

[0184] Example 32 is repeated except that 3-methoxybenzyl bromide is used as alkylating agent. Yellow solid (Yield: 38%).

Example 40:

[0185] Example 27 is repeated except that 3-methoxybenzyl bromide is used as alkylating agent. Yellow solid (Yield: 49%).

Example 41:

[0186] Example 32 is repeated except that 3-phenylbenzyl bromide is used as alkylating agent. Yellow solid (Yield: 33%).

Example 42:

[0187] Example 29 is repeated except that 3-phenylbenzyl bromide is used as alkylating agent. Orange solid (Yield: 35%).

Example 43:

[0188] Example 27 is repeated except that 3-chlorobenzyl bromide is used as alkylating agent. Yellow solid (Yield: 52%).

Example 44:

[0189] Example 27 is repeated except that 3,4-dichlorobenzyl bromide is used as alkylating agent. Yellow solid (Yield: 36%).

Example 45:

[0190] Example 29 is repeated except that 3-methoxybenzyl bromide is used as alkylating agent. Orange solid (Yield: 30 %).

Example 46:

[0191] 50.4 g (0.45 mol) of potassium tert.-butoxide, 50 g of 3-tolunitrile and 300 ml of tert.-amyl alcohol are heated up to 100°C under a nitrogen atmosphere. As soon as the this temperature is reached, a solution of 50.6 g (0.22 mol) of di-n-butyl succinate and 50 ml of tert.-amyl alcohol are added over 1 hour using a dropping funnel. When the addition is completed, the reaction mixture is kept for 19 hours at 100°C, then cooled to 65°C, neutralized with 40 ml of glacial acetic acid and boiled briefly to reflux. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 300 ml of methanol and the pigment is isolated again by filtration, then finally washed with methanol and water until washings run colourless, and dried at 100°C in an atmosphere under reduced pressure which affords

28.8 g (42% of theory, based on dibutyl succinate) of 1,4-diketo-3,6-bis-(3-methylphenyl)-pyrrolo-(3,4-c)-pyrrole. Example 29 is repeated except that 1,4-diketo-3,6-bis-(3-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Yellow solid (Yield: 34%).

5 Example 47:

[0192] Example 46 is repeated except that 3,5-dimethylbenzyl bromide is used as alkylating agent. Yellow solid (Yield: 42%).

10 Example 48:

[0193] 53 g (0.47 mol) of potassium tert.-butoxide, 50 g (0.38 mol) of 3-methoxybenzonitrile and 250 ml of tert.-amyl alcohol are heated up to 100°C under a nitrogen atmosphere. As soon as the this temperature has been reached, a solution of 50.6 g (0.22 mol) of di-n-butyl succinate and 50 ml of tert.-amyl alcohol is added over 1 hour using a dropping
15 funnel. When the addition is completed, the reaction mixture is kept for 20 hours at 100°C, then cooled to 65°C, neutralized with 35 ml of glacial acetic acid and boiled briefly to reflux. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 500 ml of water and the pigment is isolated again by filtration, then finally washed with methanol and water until washings run colourless, and dried at 100°C in an atmosphere under reduced pressure which affords 42.3 g (65% of theory, based on dibutyl succinate) of 1,4-diketo-3,6-bis-(3-methoxyphenyl)-
20 pyrrolo-(3,4-c)-pyrrole.

Example 29 is repeated except that 1,4-diketo-3,6-bis-(3-methoxyphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Yellow solid (Yield: 45%).

Example 49:

25 [0194] Example 48 is repeated except that 3,5-dimethylbenzyl bromide is used as alkylating agent. Yellow solid (Yield: 38%).

Example 50:

30 [0195] Example 32 is repeated except that 3,5-di-tert-butylbenzyl bromide is used as alkylating agent. Yellow solid (Yield: 27%).

Example 51:

35 [0196] 2.2 g (5.0 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 20 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 1.46 g (13.0 mmol) of potassium tert.-butoxide are added to the slurry under nitrogen. After stirring for 2 hours, 2.53 g (13 mmol) of neopentyl iodide is added to the reaction mixture. The mixture is heated up to 120°C and stirred additionally for 12 hours. After cooling to room temperature, the mixture is
40 poured into 50 ml of water and a red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 0.13 g (4%) of an orange solid are obtained.

Example 52:

45 [0197] 1.87 g (5.0 mmol) 1,4-diketo-3,6-bis-(4-dimethylaminophenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 60 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 1.68 g (15.0 mmol) of potassium tert.-butoxide are added to the slurry under nitrogen. After stirring for 2 hours, 2.78 g (15 mmol) of 1-bromoethyl benzene are added to the reaction mixture. The mixture is then heated up to 80°C and stirred additionally for 2 hours. After cooling to room temperature, the mixture is poured into 50 ml of water and a red solid is filtered off and purified by column chromatog-
50 raphy (silica gel, dichloromethane as eluent). After drying, 0.2 g (10%) of a red solid are obtained.

Example 53:

[0198] Example 52 is repeated except that 3,5-di-t-butylbenzyl bromide as alkylating agent. Red solid (Yield : 33%).

Example 54:

[0199] Example 52 is repeated except that 3-bromolbenzyl bromide as alkylating agent. Red solid (Yield : 23%).

Example 55:

[0200] Example 53 is repeated except that 1,4-diketo-3,6-bis-(6-methoxy-2-naphthyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Red solid (Yield : 21%).

Example 56:

[0201] Example 53 is repeated except that 1,4-diketo-3,6-bis-(4-chlorophenyl)-pyrrolo-(3,4-c)-pyrrole as starting material. Yellow solid (Yield : 25%).

Example 57:

[0202] Example 53 is repeated except that 1,4-diketo-3,6-bis-(2-naphthyl)-pyrrolo-(3,4-c)-pyrrole as starting material. Red solid (Yield : 23%).

Example 58:

[0203] Example 53 is repeated except that 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole and 1-bromo-n-propyl benzene as starting material and alkylating agent, respectively. Red solid (Yield : 5%).

Example 59:

[0204] 6.7 g (60 mmol) of potassium tert.-butoxide, 10.7 g (52 mmol) of 4-cyano-trans-stilbene and 100 ml of tert.-amyl alcohol are heated up to 100°C under a nitrogen atmosphere. As soon as the temperature is reached, a solution of 5.98g (26 mmol) of di-n-butyl succinate and 50 ml of tert.-amyl alcohol is added over 1 hour using a dropping funnel. When the addition is completed, the reaction mixture is kept for 16 hours at 100°C, then cooled down to 65°C, neutralized with 20 ml of glacial acetic acid and boiled briefly to reflux temperature. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 100 ml of methanol and the pigment is isolated by filtration, then finally washed with methanol and water until washings run colourless, and dried at 100°C in an atmosphere under reduced pressure which affords 2.5 g (20% of theory, based on dibutyl succinate) of pure pigment of 1,4-diketo-3,6-bis-(4-trans-stilbene)-pyrrolo-(3,4-c)-pyrrole. Example 53 is repeated except that and 1,4-diketo-3,6-bis-(4-trans-stilbene)-pyrrolo-(3,4-c)-pyrrole is used as starting material. Red solid (Yield: 20%).

Example 60:

[0205] Example 59 is repeated except that 3,5-dimethylbenzyl bromide as alkylating agent. Red solid (Yield : 33%).

Example 61:

[0206] Sodium hydride (60% dispersion in mineral oil, 47 g, 1.175 mol) is added portionwise over a 30-minutes period without external cooling and under nitrogen to a slurry of 1,4-diketo-3,6-bis-(4'-biphenyl)pyrrolo[3,4-c]pyrrole (140 g, 0.318 mol, obtained according to example 19 of US 4,579,949) in 1-methyl-2-pyrrolidone (2 liters). After two hours the reaction mixture is cooled in an ice-water bath for 30 minutes, then benzyl bromide (216 g, 1.263 mol) is added dropwise (over 30 minutes). The reaction mixture is then slowly warmed-up to room temperature (by keeping the reaction flask in the cooling bath and allowing the ice in the bath to melt) and stirred at this temperature for 60 hours. Then acetic acid (50 ml), water (50 ml) and acetone (1.5 liters) are successively added. After stirring for one hour, a red solid is filtered off, washed with acetone (500 ml), water (4 liters), ethanol (1 liter), hexane (1 liter) and acetone (500 ml) and then dried under an atmosphere of reduced pressure at 50°C for 24 hours. Yield: 129.50 g (66%) of bright red solid 1,4-diketo-2,5-dibenzyl-3,6-bis-(4'-biphenyl)pyrrolo[3,4-c]pyrrole.

Elemental analysis: C: 83.05% (calc. 85.14%), H: 5.36% (calc. 5.20%), N: 4.15% (calc. 4.51%), max. absorbance (solid state): 497 nm; max. fluorescence (solid state): 557 nm; absorption (max) in toluene (aerated): 492 nm; fluorescence (max) in toluene (aerated): 557 nm; molar absorption coefficient (in toluene): 27579; quantum yield (in toluene): 0.50.

Example 62:

[0207] Example 61 is repeated except that of 1,4-diketo-3,6-bis-(4-methylphenyl)pyrrolo[3,4-c]pyrrole as starting material Red solid (Yield : 42%).

Example 63:

[0208] Example 53 is repeated except that 1,4-diketo-3,6-bis-(4-cis-stilbene)-pyrrolo-(3,4-c)pyrrole is used as starting material. Red solid (Yield : 36%).

Example 64:

[0209] Example 36 is repeated except that 3-phenylbenzyl bromide as alkylating agent. Red solid (Yield : 25%).

Example 65:

[0210] Example 46 is repeated except that 1-phenylethyl bromide as alkylating agent. Red solid (Yield : 11%).

Example 66:

[0211] Example 61 is repeated except that 3,5-di-t-butylbenzyl bromide as alkylating agent. Red solid (Yield : 11%).

Example 67:

[0212] Example 48 is repeated except that 3,5-di-t-butylbenzyl bromide as alkylating agent. Red solid (Yield : 42%).

Example 68:

[0213] To the below mentioned engineering plastics (each 400 g) in chip form the inventive compounds (each 0.12 g) are added in a paint shaker and shaken there for 90 seconds. Thereafter, the thus obtained chips comprising the adhered inventive compounds are molded at the temperatures specified in Table 1 below using a BA400 Battenfeld injection molder.

Table 1

Engineering plastic	Temperature settings (°C)		
	Nozzle	Middle	Rear
HIPS	232 (450°F)	232 (450°F)	232 (450°F)
ABS	232 (450°F)	232 (450°F)	232 (450°F)
Nylon 6,12	271 (520°F)	260 (500°F)	254 (490°F)
PMMA	226 (440°F)	226 (440°F)	226 (440°F)
HIPS : high impact polystyrene (825P1 from Fina Oil and Chemical; melt flow (g/10 min): 8 (reference ASTM TEST 200/5.0 D-1238))			
ABS : acrylic-butadiene-styrene copolymer (Natural ABS 3501-002 from Diamond Polymer; melt flow (g/10 min): 7.5 (reference ASTM Method D-1238))			
Nylon 6,12 : polyamide (ZYTEL®158L from DuPont Engineering Polymers; inherent viscosity: 1.15))			
PMMA: polymethylmethacrylate (PLEXIGLAS®V825 from Atohaas; melt flow (g/10 min): 3.7 (reference ASTM Method D-1238))			

[0214] Five chips (from the same series) obtained from the injection molder are collected after the color is distributed homogeneously.

[0215] The color chips are then mounted, with the thickest part of the chip exposed (0.31 cm (0.122 inches)), in a CI35A Atlas Xenon Weather-O-Meter. The parameters of the weather-o-meter are listed in Table 2.

[0216] The color chips are then exposed to the weather-o-meter for 100, 250, 500, 750, and 1000 hours. The color chips are rated after each fading interval is reached. The lightfastness is subjectively evaluated using a gray scale rating of 1-5. A rating of 5 indicates no fade or color difference. In cases where the color chip appears to darken a rating of d for darkening is applied to the gray scale rating. In cases where the color chip loses most of its color a rating of f for fading is applied to the gray scale rating.

Table 2:

Parameters for the fading test	
Automatic voltage 0.35 W/m ² at 340 nm	
	Light Cycle Settings
	Temperature [°C]
Black Panel ¹⁾	63
Wet Bulb Depression ²⁾	10
Conditioning Water ³⁾	30

automatic voltage: controls irradiance level (similar to the average irradiance found on a clear summer day in southern Florida)

1) temperature is measured by a sensor attached to the specimen holder; provides a temperature reading resulting from the chamber air and any heating due to the xenon light

2) difference between air temperature (measured by the so-called dry bulb sensor) and wet bulb temperature (measured by wet bulb sensor, whereby the wet bulb is covered by a moistened wick; due to the cooling effect of evaporation, the wet bulb reading is usually lower than the dry bulb reading (except at 100% relative humidity)).

RESULTS

[0217]

Table 3:

Nylon evaluation					
used DPP of example no.	Lightfastness evaluation using the gray scale				
	100 h	250 h	500 h	700 h	1000 h
5	4/5	4/5d	3/4d	3/4d	3/4d
7	4/5	4/5d	4f	3/4f	2/3f
4	4/5	4d	3/4d	3/4d	3/4d
(gray scale assesses color differences after exposure to light, from 1 to 5, wherein 5 means no change in color)					

[0218] By comparison, the commercial thioindigo Vat Red 41 (Hostasol® Red 5B from Clariant) decomposed in nylon, i.e. no color is found in the produced nylon chips.

Table 4:

PMMA evaluation					
Used DPP of example no.	Lightfastness evaluation using the gray scale				
	100 h	250 h	500 h	700 h	1000 h
4	5	5	4/5	4/5	4/5
5	5	5	4/5	4/5	4/5
7	5	5	4/5	4/5	4/5
11	5	4/5	4/5	4/5	4/5
13b	5	4/5	4/5	4/5	4/5
15	5	4d	4	3	3f
Vat Red 41	3f	2f	1f at 322 h		

Table 5:

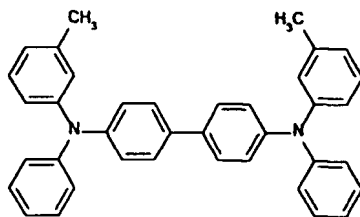
ABS evaluation					
Used DPP of example no.	Lightfastness evaluation using the gray scale				
	100 h	250 h	500 h	700 h	1000 h
4	4/5	4/5	4/5d	4d	4d
5	4	4	4d	4d	4d
7	4	4d	4d	4d	4d
11	4/5	4/5	4/5d	4/5d	4d
13b	4/5	4/5	4/5d	4/5d	4d
15	4/5	3/4d	3/4d	3d	3d
Vat Red 41	3	2	1f at 322h		

Table 6:

HIPS evaluation					
used DPP of example no.	Lightfastness evaluation using the gray scale				
	100 h	250 h	500 h	700 h	1000 h
4	4/5	4	4	4d	3d
5	4	4	3/4	3d	2/3d
7	4	4	3/4	3d	2/3d
10d	4/5	4	4d	3d	3d
11	4/5	4/5	4	4	3/4d
13b	4/5	4/5	4/5d	4d	3/4d
15	4/5	3/4d	3/4d	3d	3d
Vat Red 41	3	2/3	1f		

Example 69:

[0219] On an ITO glass substrate (from Geomatech Co. Ltd., ITO film thickness 200 nm, sheet resistance $10 \Omega/\text{cm}^2$), the TPD compound of the following formula



is deposited as a hole transporting substance by vacuum evaporation under a reduced pressure of 6.665×10^{-4} Pa (5.0×10^{-6} Torr) and at a depositing rate of 0.05 nm/sec to a membrane thickness of 50 nm to form a hole transporting layer. Then, on the hole transporting layer thus prepared, the compound of Example 1 is deposited as a light-emitting material under a depositing condition of 6.665×10^{-4} Pa (5.0×10^{-6} Torr) and 0.05 nm/sec to a membrane thickness of 50 nm to form a light-emitting layer. Then, on the light-emitting layer, firstly lithium is co-deposited with the above compound at a rate of 0.015 nm/sec to form a 1 nm-thick layer and subsequently aluminum as cathode are deposited on it to a film thickness of 200 nm. By using the ITO side as the anode and the aluminum side as the cathode, a bias

of 20 V is applied to the above element. A luminescence showing a luminance of 1410 cd/m² with the EL emission peak wavelength at 560 nm is confirmed as the average value of the five elements. For evaluation of luminance and emission spectrum, the Luminometer BM-8 manufactured by TOPCON Co., Ltd. and the Multichannel Photodetector IMUC-7000 manufactured by Otsuka Electronics are used, respectively.

Example 70 - 101:

[0220] Example 69 is repeated replacing the light-emitting material with the compounds indicated in Table 7 below, summarizing the EL performances also (the results of Example 69 is included also in the table).

Table 7

Example	Light-emitting Material (Example)	EL Emission-Peak Wavelength (nm)	EL Intensity (cd/m ²)
69	1	560	1410
70	2	580	408
71	5	573	662
72	7	580	157
73	11	581	596
74	12	578	1184
75	13	581	4680
76	14	576	3030
77	15	570	1932
78	16	574	2310
79	17	569	2990
80	18	578	2670
81	19	566	5260
82	20	581	1563
83	21	568	4110
84	22	579	1303
85	23	579	3970
86	24	585	3340
87	25	584	430
88	26	581	398
89	29	578	2810
90	30	577	1473
91	31	579,619	27
92	33	568	202
93	34	534	2600
94	35	585	1842
95	37	581	2220
96	39	552	1648
97	40	576	1976
98	43	576	772
99	45	575	1334

Table 7 (continued)

Example	Light-emitting Material (Example)	EL Emission-Peak Wavelength (nm)	EL Intensity (cd/m ²)
100	61	578	1863
101	62	557	1516

Example 102:

[0221] The compounds of examples 14, 15, 16, 17, 19, 21 and 39 are weighed precisely in 0.1 mg-order and dissolved in 50ml toluene (aerated) using volumetric flask to give exact solution molarity. Optical absorption spectra thereof are measured using HITACHI U-3300 spectrophotometer to evaluate molar absorption coefficient. The solutions are then precisely diluted by 10-times with aerated toluene using measuring pipette and volumetric flask. Optical absorption and photoluminescence spectra of the above diluted solutions are measured using U-3300 and HITACHI F-4500 fluorescence spectrophotometer, respectively, to evaluate FQY.

[0222] The above compounds are deposited on a slide glass substrate by vacuum evaporation under a reduced pressure of 6.665×10^{-4} Pa (5.0×10^{-6} Torr) and at a depositing rate of 0.05nm/sec to a film thickness of 50nm to form a transparent film. Optical absorption and photoluminescence spectra of the films are evaluated using U-3300 and F-4500 spectrophotometer, respectively. The results are summarized in the table below. These compounds absorb the light of approximately 480nm in both solution state and evaporated film and fluoresce in green region in solution and fluoresce in orange to red region in evaporated film. These properties prove that the compounds are applicable for color changing media described previously.

Table 8:

use for color changing media						
compound of example	in toluene				in evaporated film	
	λ_{ma}^*1 , nm	ϵ^*2	F_{max}^*3 , nm	Φ^*4	λ_{max}^*1 , nm	F_{max}^*3 , nm
14	479	21480	531	0.65	478	598
15	474	23060	529	0.67	476	589
16	486	20150	529	0.65	484	592
17	474	10310	529	0.72	481	588
19	474	21870	530	0.61	480	586
21	476	22320	530	0.60	490	608
39	475	13950	528	0.65	480	581

*1 : wavelength at optical absorption maximum

*2 : molar absorption coefficient

*3 : wavelength at photoluminescence maximum

*4 : FQY

Example 103:

[0223] example 69 is repeated replacing the light-emitting material and the cathode with the film co-deposited using the compound described in example 34 and Rhodamine-19 (0.50 wt.-%) and the cathode co-deposited using magnesium and silver (Mg:Ag, 20:1), respectively. The co-deposition is done under a depositing condition of 6.665×10^{-4} Pa (5.0×10^{-6} Torr) and 0.13 nm/s (1.3Å/s) for the compound of example 34, 0.66 pm/s (0.0066Å/s) for Rhodamine-19, 200 pm/s (2.0Å/s) for magnesium and 10 pm/s (0.1Å/s) for silver. For comparison, the device employing the compound of example 34 for light-emitting substance is prepared using the cathode of Mg/Ag (20:1).

[0224] The device possessing the co-deposited light-emitting layer begins to emit from at 4V. The wavelength of the EL emission spectrum is 558nm. This suggests that the emission is induced via resonance energy transfer from the compound of example 34 to Rhodamine-19. The device of the single component light-emitting layer begins from at 7V with the maximum EL emission wavelength 529 nm. The EL emission performances are summarized in the table below.

Bias voltage (V)	EL Intensity (cd/m ²)	
	Host-Guest type	Single component type
12	290	12
13	600	36
14	1220	67
15	1900	135

[0225] The above results demonstrate that the invented compounds are useful for Host-Guest type light-emitting materials.

Example 104:

[0226] 28 g (0.25 mol) of potassium tert.-butoxide, 62.5g (0.23 mol) of 4-(diphenylamino)benzonitrile and 300 ml of tert.-amyl alcohol are heated up to 100°C under a nitrogen atmosphere. As soon as the this temperature has been reached, a solution of 26.7 g (0.12 mol) of di-n-butyl succinate and 70 ml of tert.-amyl alcohol is added over 1 hour using a dropping funnel. When the addition is completed, the reaction mixture is kept for 16 hours at 100°C, then cooled down to 65°C, neutralized with 20 ml of glacial acetic acid and boiled briefly at reflux temperature. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 300 ml of methanol and the pigment is isolated again by filtration, then finally washed with methanol and water until washings run colourless, and dried at 100°C in vacuo, affording 10.8 g (15% of theory, based on dibutyl succinate) of pure pigment of 1,4-diketo-3,6-bis-(4-diphenylaminophenyl)-pyrrolo-(3,4-c)-pyrrole.

[0227] 1.02 g (1.64 mmol) 1,4-diketo-3,6-bis-(4-diphenylaminophenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 20 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 0.57g (5.09 mmol) of potassium tert.-butoxide is added to the slurry under nitrogen. After stirring for 2 hours, 1.37 g (4.84 mmol) of 3,5-di-*t*-butylbenzyl bromide are added to the reaction mixture and then the mixture is stirred additionally for 2 hours. After the reaction mixture is poured into 50 ml of water, the obtained solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 0.444 g (26%) of a red solid are obtained.

[0228] The compound obtained above exhibits the optical properties summarized in the table below:

in toluene				in evaporated film	
λ_{\max} ^{*1} nm	ϵ ^{*2}	F_{\max} ^{*3} nm	Φ ^{*4}	λ_{\max} ^{*1} nm	F_{\max} ^{*3} nm
533	47400	591	0.48	537	609

*1: wavelength at optical absorption maximum,

*2: molar absorption coefficient

*3: wavelength at photoluminescence maximum,

*4: FQY

[0229] Example 103 is then repeated for EL device preparation replacing the light-emitting material with the film co-deposited using tris-(8-hydroxyquinolato)aluminum(III) (manufactured by Wako Pure Chemicals Industries, Ltd.) and the compound prepared above (0.50 wt.-%). The co-deposition is done under a depositing condition of 6.665×10^{-4} Pa (5.0×10^{-6} Torr) and 300 pm/s (3.0 Å/s) for the aluminum complex and 1.5 pm/s (0.015 Å/s) for the above compound. For comparison, the device employing the aluminum complex for light-emitting substance is prepared.

[0230] The device using a light-emitting layer comprising of solely the aluminum complex begins to emit a green EL emission starting at 8 V. The emission maximum is at 520 nm with the intensity 6980 cd/m² at 25 V. The device using a light-emitting layer comprising the complex and the compound begins to emit from at 4 V (see the table below for the device performance). The wavelength of the EL emission maximum is at 590 nm, i.e. orange emission which is different from that of the single component device above. This suggests that the emission is induced via resonance energy transfer from the aluminum complex to the compound invented.

Bias voltage (V)	EL Intensity (cd/m ²)
15	540

(continued)

Bias voltage (V)	EL Intensity (cd/m ²)
16	1300
17	3900
18	12520

[0231] The above results demonstrate that the invented compounds are useful for energy acceptor of Host-Guest type of light-emitting materials.

Example 105:

[0232] 2.09 g (4.75 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 30 ml of 1-methyl-2-pyrrolidinone for 2 hours at room temperature. 1.29 g (11.52 mmol) of potassium tert.-butoxide are added to the slurry under an atmosphere of nitrogen. After stirring for 1 hour, 1.21 g (10 mmol) of allyl bromide are added to the reaction mixture and then the mixture is stirred additionally for two hours. The mixture then is poured into 50 ml of water and the obtained red solid is filtered off and then purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 1.13 g (60%) of a red solid are obtained.

Example 106:

[0233] Example 105 is repeated except that 1,4-diketo-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting material. A red solid (54%) is obtained.

Example 107:

[0234] Example 105 is repeated except that 3,3-dimethylallyl bromide is used instead of allyl bromide. A red solid (42%) is obtained.

Example 108:

[0235] Example 105 is repeated except that 3-phenylallyl bromide is used instead of allyl bromide. A red solid (55%) is obtained.

Example 109:

[0236] A mixture of 45 g (0.4 mol) of potassium tert.-butoxide, 82 g (0.373 mol) of 9-ethyl-3-cyanocarbazole and 300 ml of tert.-amylalcohol is heated up to a temperature of 110°C under a nitrogen atmosphere. As soon as this temperature is reached, a solution of 43 g (0.18 mol) of di-n-butyl succinate and 100 ml of tert.-amyl alcohol are added over 1.5 hours using a dropping funnel. When the addition is complete, the reaction mixture is kept for 16 hours at 110°C, then cooled to 65°C, neutralized with 40 ml glacial acetic acid and boiled briefly at reflux temperature. The resultant pigment suspension is filtered at room temperature. The filter cake is suspended in 300 ml of methanol and the pigment is isolated by filtration, then finally washed with methanol and water until washings run colorless, and dried at 100°C under an atmosphere of reduced pressure. 10.5 g (11%) of pure 1,4-diketo-3,6-bis-(3-9-ethylcarbazole)-pyrrolo-(3,4-c)-pyrrole are obtained.

Example 110:

[0237] Example 105 is repeated except that 1,4-diketo-3,6-bis-(2-naphthyl)-pyrrolo-(3,4-c)-pyrrole and 3,5-di-tert.-butylbenzylbromide are used. A red solid (36%) is obtained.

Example 111:

[0238] Example 110 is repeated except that 3,5-dimethylbenzyl bromide is used instead of 3,5-di-tert.-butylbenzylbromide. A red solid (30%) is obtained.

Example 112:

[0239] Example 109 is repeated except that 1-(4-cyanophenyl)-2-(3,5-di-tert.-butylphenyl)-trans-ethylene is used instead of 9-ethyl-3-cyanocarbazole. A red solid (5%) is obtained.

Example 113:

[0240] Example 112 is repeated except that 3,5-dimethylbenzyl bromide is used as alkylating agent. A red solid (8%) is obtained.

Example 114:

[0241] Example 10 is repeated except that 3-bromo benzyl bromide as alkylating agent. A red solid (23%) is obtained.

Example 115:

[0242] Example 10 is repeated except that methyl iodide is used as alkylating agent. A red solid (40%) is obtained.

Example 116:

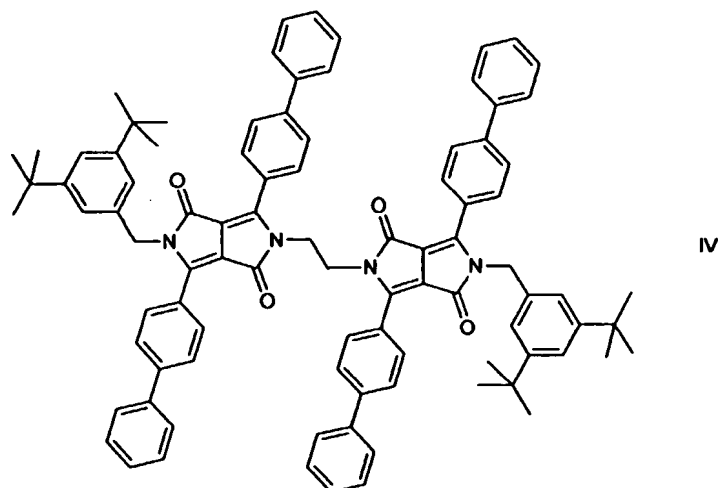
[0243] Example 10 is repeated except that 3-methylbenzyl bromide is used as alkylating agent. A red solid (45%) is obtained.

Example 117:[0244]

(a) 4.04 g (10 mmol) 1,4-diketo-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 30 ml of 1-methyl-2-pyrrolidinone for two hours at room temperature. 1.23 g (11 mmol) of potassium tert.-butoxide are added to this slurry under a nitrogen atmosphere. After stirring for 1 hour, 2.83 g (10 mmol) of 3,5-di-tert.-butylbenzylbromide is added to the reaction mixture and then the mixture is stirred additionally for two hours. The mixture is poured into 50 ml of water and the red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 1.61 g (25%) 1,4-diketo-2-(di-tert.-butylbenzyl)-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are obtained.

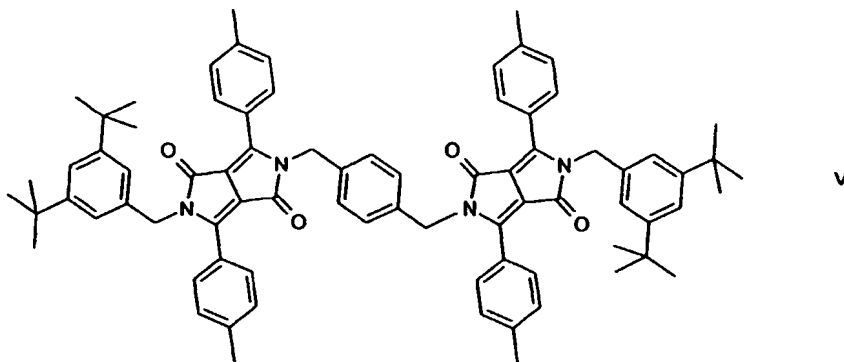
(b) The obtained 1.61 g 1,4-diketo-2-(di-tert.-butylbenzyl)-3,6-bis-(4-biphenyl)-pyrrolo-(3,4-c)-pyrrole are slurred in 20 ml of 1-methyl-2-pyrrolidinone for 15 min. at room temperature.

[0245] 0.32 g (2.8 mmol) of potassium tert.-butoxide are added to the slurry under a nitrogen atmosphere. After stirring for one hour, 3.38 g (1.2 mmol) of 1,2-diiodoethane are added to the reaction mixture and then the mixture is stirred additionally for two hours. Then the mixture is poured into 50 ml of water and the red solid is filtered off and purified by column chromatography (silica gel, dichloromethane as eluent). After drying, 0.58 g of a red solid of formula IV are obtained

**Example 118:****[0246]**

(a) Example 117 (a) is repeated except that 1,4-diketo-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is used as starting compound and 1,4-diketo-2-(di-tert.-butylbenzyl)-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole is obtained (32%).

(b) Example 117 (b) is repeated except that 1,4-diketo-2-(di-tert.-butylbenzyl)-3,6-bis-(4-methylphenyl)-pyrrolo-(3,4-c)-pyrrole and a,a'-dibromo-p-xylene are used. A red solid of the following formula V



is obtained.

Examples 119 to 129:

[0247] Example 104 is repeated replacing only the guest material in the binary system with the compounds listed in Table 9 below, summarizing the EL performances also:

Table 9

Example	Guest Material (example)	Guest Concentration [wt.-%] to Alq ₃	EL Emission Peak Wavelength [nm]	EL Intensity [cd/m ²]
119	57	1.4	555	4820

Table 9 (continued)

Example	Guest Material (example)	Guest Concentration [wt.-%] to Alq ₃	EL Emission Peak Wavelength [nm]	EL Intensity [cd/m ²]
120	53	1.2	594	8517
121	55	1.3	566	7329
122	59	1.8	591	5344
123	104	1.3	608	11004
124	114	1.5	619	9831
125	109	1.3	567	8745
126	112	1.8	591	5302
127	115	1.4	611	6398
128	116	2	617	8784
129	10	2	621	7108

Example 130 to 134:

[0248] Example 69 is repeated replacing the light emitting material with the compounds listed in Table 10 below, summarizing the EL performances also:

Table 10

Example	Guest Material (example)	EL Emission Peak Wavelength [nm]	EL Intensity [cd/m ²]
130	105	639	1429
131	106	611	4540
132	109	588, 625	2330
133	112	605	1654
134	113	624	875

Example 135:

[0249] 294 mg of in tetrahydrofuran recrystallized Alq₃ (manufactured from Tokyo Kasei Organic Chemicals) and 6 mg of 1,4-diketo-2,5-bis-(3,5-di-tert.-butylbenzyl)-3,6-bis-(4-diphenylaminophenyl)-pyrrolo-(3,4-c)pyrrole are dissolved in 50 ml of dichloromethane. The thus obtained solution is slowly poured into 500 ml of hot water, and the thus obtained precipitate is collected and dried. The obtained precipitate is purified by means of sublimation with heating under an atmosphere of reduced pressure of $6.65 \cdot 10^{-4}$ Pa ($5 \cdot 10^{-6}$ Torr). 250 mg (5%) of a red host/guest composite are obtained.

[0250] Example 103 is then repeated for EL device preparation replacing the light-emitting material with the above obtained host/guest composite.

Examples 136 to 138:

[0251] Example 136 is repeated without a replacement of the guest concentration listed in Table 11 below:

Table 11

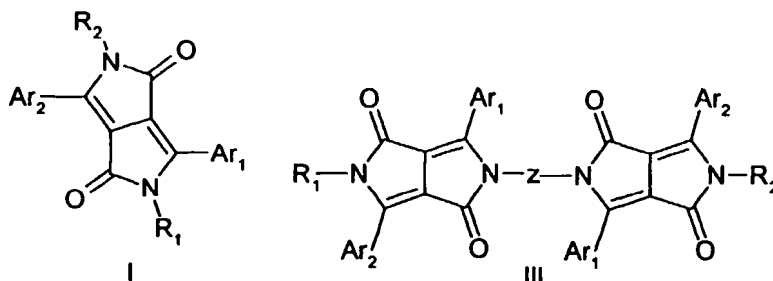
Example	Guest Concentration [wt.-%]	EL Emission Peak Wavelength [nm]	EL Intensity [cd/m ²]
136	5	615	9013
137	3	617	10085
138	2	613	9686

Claims

1. Electroluminescent device comprising in this order

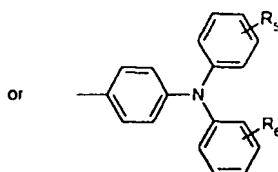
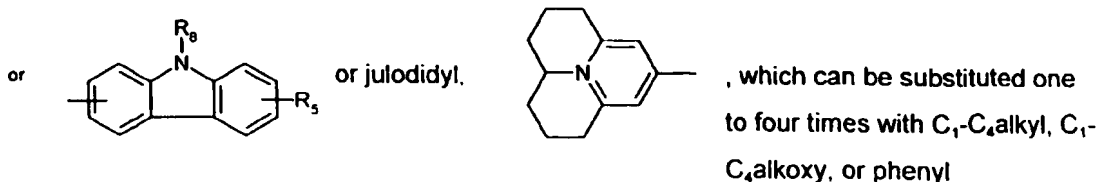
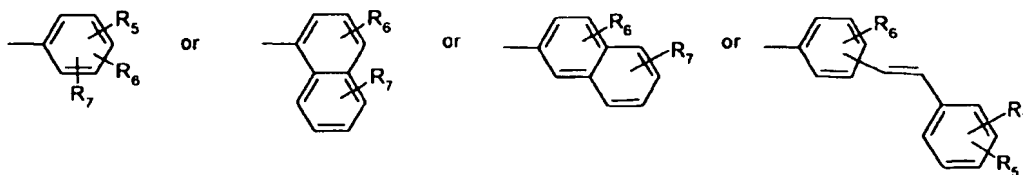
- (a) an anode
 (b) a hole transporting layer
 (c) a light-emitting layer
 (d) optionally an electron transporting layer and
 (e) a cathode

and a light-emitting substance, wherein the light-emitting substance is a diketopyrrolopyrrole ("DPP") represented by formula I or formula III



wherein R_1 and R_2 , independently from each other, stand for C_1 - C_{25} -alkyl, allyl which can be substituted one to three times with C_1 - C_3 alkyl or Ar_3 , or $-CR_3R_4-(CH_2)_m-Ar_3$, wherein R_3 and R_4 independently from each other stand for hydrogen or C_1 - C_4 alkyl, or phenyl which can be substituted one to three times with C_1 - C_3 alkyl, Ar_3 stands for phenyl or 1- or 2-naphthyl which can be substituted one to three times with C_1 - C_8 alkyl, C_1 - C_8 alkoxy, halogen or phenyl, which can be substituted with C_1 - C_8 alkyl or C_1 - C_8 alkoxy one to three times, and m stands for 0, 1, 2, 3 or 4,

Ar_1 and Ar_2 , independently from each other, stand for aryl radicals, preferably for



wherein

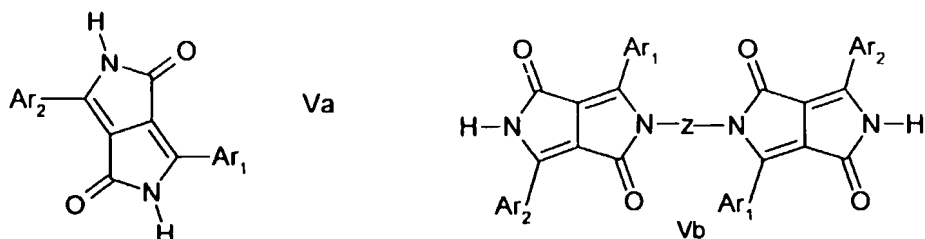
R_5 , R_6 and R_7 , independently from each other, stand for hydrogen, cyano, halogen, C_1 - C_6 alkyl, $-NR_8R_9$, $-OR_{10}$, $-S(O)_nR_8$, $-Se(O)_nR_8$, or phenyl, which can be substituted one to three times with C_1 - C_8 alkyl or C_1 - C_8 alkoxy,

wherein R_8 and R_9 , independently from each other, stand for hydrogen, phenyl, C_1 - C_{25} alkyl, C_5 - C_{12} -cycloalkyl, $-CR_3R_4-(CH_2)_m-Ph$, R_{10} , wherein R_{10} stands for C_6 - C_{24} -aryl, or a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein Ph, the aryl and heterocyclic radical can be substituted one to three times with C_1 - C_8 alkyl, C_1 - C_8 alkoxy, or halogen, or R_8 and R_9 stand for $-C(O)R_{10}$, wherein R_{11} can be C_1 - C_{25} alkyl, C_5 - C_{12} -cycloalkyl, R_{10} , $-OR_{12}$ or $-NR_{13}R_{14}$, wherein R_{12} , R_{13} , and R_{14} stand for C_1 - C_{25} alkyl, C_5 - C_{12} -cycloalkyl, C_6 - C_{24} -aryl,

or
a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein the aryl and heterocyclic radical can be substituted one to three times with C_1 - C_8 alkyl or C_1 - C_8 alkoxy, or $-NR_8R_9$ stands for a five- or sixmembered heterocyclic radical in which R_8 and R_9 together stand for tetramethylene, pentamethylene, $-CH_2-CH_2-O-CH_2-CH_2-$, or $-CH_2-CH_2-NR_5-CH_2-CH_2-$, preferably $-CH_2-CH_2-O-CH_2-CH_2-$, and n stands for 0, 1, 2 or 3,

and wherein Z stands for a diradical selected from the group consisting of a single bond, C_2 - C_6 alkylene, which can be substituted one to three times with C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or phenyl, phenylene or naphthylene.

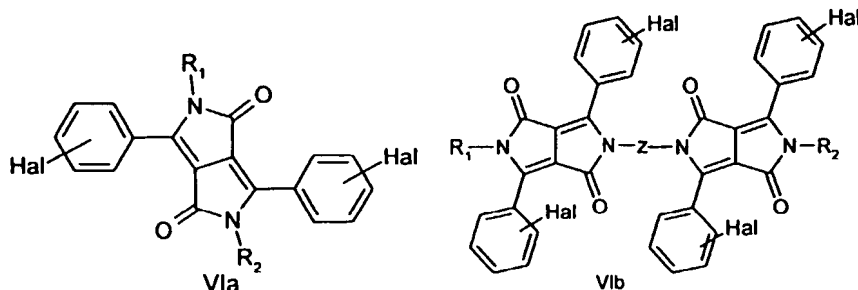
2. Process for the preparation of compounds I or III according to claim 1 in treating in a first step the DPP derivative of formula Va or formula Vb



wherein Ar_1 and Ar_2 are defined as in claim 1, with a base, then, in a second step, treating the reaction mixture obtained in the first step with an usual alkylating agent, wherein in the first step the base is a hydride, an alkali metal alkoxide or a carbonate, and the alkylating agent is a sulfonate, tosylate, mesylate, carbonate, sulfate, or halogen compound of the formula $(R_1)_{1 \text{ or } 2}X$, wherein X stands for SO_3^- , $(p\text{-Me-phenyl})SO_2^-$, $(2,4,6\text{-trimethyl-phenyl})SO_2^-$, $-CO_3^-$, $-SO_4^-$, or halogen, or a mixture of $(R_1)_{1 \text{ or } 2}X$ and $(R_2)_{1 \text{ or } 2}X$.

3. Process for the preparation of compounds I or III according to claim 1

(a) in treating in a first step the DPP derivative of formula VIa or formula VIb



wherein R_1 and R_2 are defined as in claim 1, Hal stands for halogen, with a nucleophilic agent such as a secondary amine, HNR_8R_9 , a thiol, HSR_8 , or $HS(O)_nR_8$, an alcohol, HOR_{10} , a diselenide, $R_8(O)_nSe-Se(O)_nR_8$, preferably in a molar ratio of DPP VIa or VIb:nucleophilic agent in the range of 1.2:1 to 0.8:1, or, if R_2 has the

same meaning as R_1 in the range of from 1:2.5 to 1:1, in the presence of an anhydrous dipolar aprotic solvent, and of an anhydrous base in an amount in the range of from usually 0.1 to 15 moles per mole of the nucleophilic agent, at a temperature in the range of from usually 100 to 220°C and under a pressure generally in the range of from 100 to 300 kPa, and optionally isolating the obtained compound Va, resp. Vb,

(b) then treating the obtained compound Va, resp. Vb (as defined in claim 2), with a base, thereafter in a second step, treating the reaction mixture obtained in the first step of (b) with an usual alkylating agent, wherein in the first step of (b) the base is a hydride, an alkali metal alkoxide or a carbonate, and the alkylating agent is a sulfonate, tosylate, mesylate, carbonate, sulfate, or halogen compound of the formula $(R_1)_1$ or $_2X$, wherein X stands for SO_3^- , (p-Me-phenyl)- SO_2^- , (2,4,6-trimethyl-phenyl) SO_2^- , $-CO_3^-$, $-SO_4^-$, or halogen, or a mixture of $(R_1)_1$ or $_2X$ and $(R_2)_1$ or $_2X$.

4. Method of coloring high molecular weight organic materials by incorporating the DPP compounds I or III according to claim 1 into said materials in analogy to known methods in the art.

5. Composition comprising

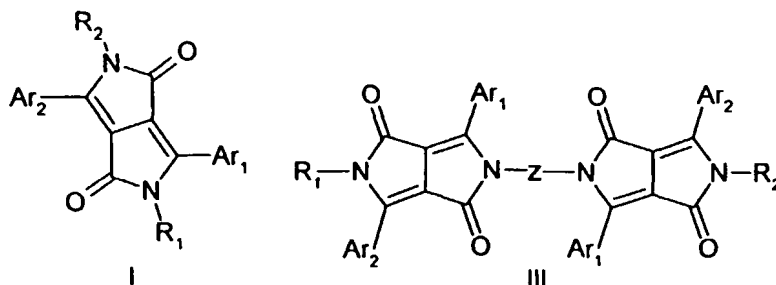
(a) 0.01 to 50% by weight, based on the total weight of the colored high molecular weight organic material, of a fluorescent DPP I or III according to claim 1, and

(b) 99.99 to 50% by weight, based on the total weight of the colored high molecular weight organic material, of a high molecular organic material, and

(c) if desired, customary additives in effective amounts.

6. Composition according to claim 6, wherein the high molecular weight organic material is a polyamide, a polystyrene, preferably high impact polystyrene, polymethylmethacrylate or an ABS copolymer.

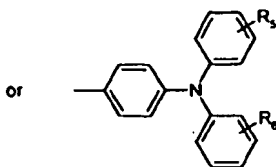
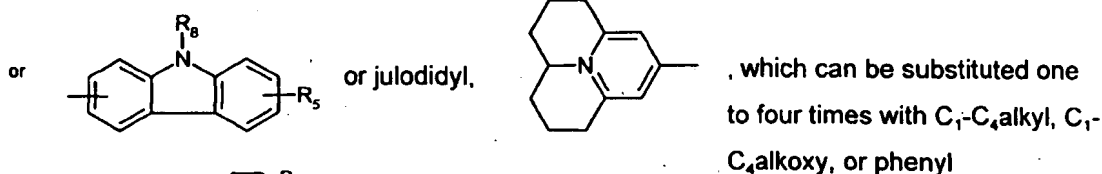
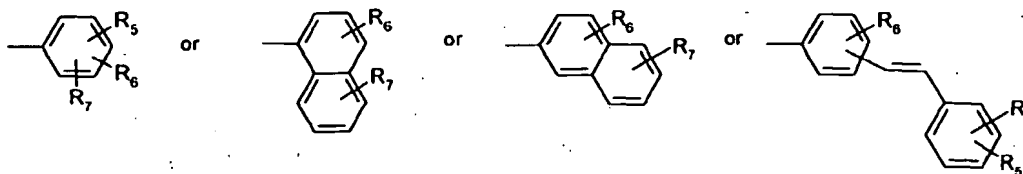
7. Fluorescent diketopyrrolopyrroles represented by formula I or formula III



wherein R_1 and R_2 , independently from each other, stand for C_1 - C_{25} -alkyl, allyl which can be substituted one to three times with C_1 - C_3 alkyl or Ar_3 , or $-CR_3R_4-(CH_2)_m-Ar_3$, wherein R_3 and R_4 independently from each other stand for hydrogen or C_1 - C_4 alkyl, or phenyl which can be substituted one to three times with C_1 - C_3 alkyl,

Ar_3 stands for phenyl or 1- or 2-naphthyl which can be substituted one to three times with C_1 - C_8 alkyl, C_1 - C_8 alkoxy, halogen or phenyl, which can be substituted with C_1 - C_8 alkyl or C_1 - C_8 alkoxy one to three times, and m stands for 0, 1, 2, 3 or 4,

Ar_1 and Ar_2 , independently from each other, stand for aryl radicals, preferably for



wherein

R₅, R₆ and R₇, independently from each other, stand for hydrogen, cyano, halogen, C₁-C₆alkyl, -NR₈R₉, -OR₁₀, -S(O)_nR₈, -Se(O)_nR₈, or phenyl, which can be substituted one to three times with C₁-C₈alkyl or C₁-C₈alkoxy,

25 wherein R₈ and R₉, independently from each other, stand for hydrogen, phenyl, C₁-C₂₅alkyl, C₅-C₁₂cycloalkyl, -CR₃R₄-(CH₂)_m-Ph, R₁₀, wherein R₁₀ stands for C₆-C₂₄aryl, or a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein Ph, the aryl and heterocyclic radical can be substituted one to three times with C₁-C₈alkyl, C₁-C₈alkoxy, or halogen, or R₈ and R₉ stand for -C(O)R₁₀, wherein R₁₁ can be C₁-C₂₅alkyl, C₅-C₁₂cycloalkyl, R₁₀, -OR₁₂ or -NR₁₃R₁₄, wherein R₁₂, R₁₃, and R₁₄ stand for C₁-C₂₅alkyl, C₅-C₁₂cycloalkyl, C₆-C₂₄aryl,

or

35 a saturated or unsaturated heterocyclic radical comprising five to seven ring atoms, wherein the ring consists of carbon atoms and one to three hetero atoms selected from the group consisting of nitrogen, oxygen and sulfur, wherein the aryl and heterocyclic radical can be substituted one to three times with C₁-C₈alkyl or C₁-C₈alkoxy, or -NR₈R₉ stands for a five- or sixmembered heterocyclic radical in which R₈ and R₉ together stand for tetramethylene, pentamethylene, -CH₂-CH₂-O-CH₂-CH₂-, or -CH₂-CH₂-NR₅-CH₂-CH₂-, preferably -CH₂-CH₂-O-CH₂-CH₂-, and n stands for 0, 1, 2 or 3,

40 and wherein Z stands for a diradical selected from the group consisting of a single bond, C₂-C₆alkylene, which can be substituted one to three times with C₁-C₄alkyl, C₁-C₄alkoxy, or phenyl, phenylene or naphthylene, with the proviso that R₆ and R₇ do not stand simultaneously for hydrogen.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 81 0848

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCl.7)
D,X	EP 0 499 011 A (JAPAT LTD) 19 August 1992 (1992-08-19) * example 3 *	1,2,4,5,7	C09K11/06 H05B33/14 C08K5/3415 C07D487/04 C09B57/00
X	EP 0 563 009 A (JAPAT LTD) 29 September 1993 (1993-09-29) * example 9 *	1,7	
D,X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 072 (C-0808), 20 February 1991 (1991-02-20) & JP 02 296891 A (RICOH CO LTD), 7 December 1990 (1990-12-07) * abstract; example 1 *	7	
A		1	
D,X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 145 (C-1178), 10 March 1994 (1994-03-10) & JP 05 320633 A (SUMITOMO CHEM CO LTD), 3 December 1993 (1993-12-03) * page 4, molecules (4) and (5) * * abstract *	1,7	
D,X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 003448 A (TOYO INK MFG CO LTD), 7 January 1997 (1997-01-07) * page 6, molecules (13), (14), (15), (16) and (17) * * abstract *	7	
A		1	
D,X	EP 0 133 156 A (CIBA GEIGY AG) 13 February 1985 (1985-02-13) * page 11 - page 15; examples 1-8,15-18 *	2-7	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		30 November 2000	Shade, M
CATEGORY OF CITED DOCUMENTS			
<p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p>			
<p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/02 (P4C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 00 81 0848

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,A	EP 0 353 184 A (CIBA GEIGY AG) 31 January 1990 (1990-01-31) * examples 1-7 *	3	
X	EP 0 811 625 A (CIBA GEIGY AG) 10 December 1997 (1997-12-10) * example 8 *	7	
X	WO 98 25927 A (CIBA GEIGY AG) 18 June 1998 (1998-06-18) * examples 1,2,4-16,19-31 *	2,7	
X	WO 96 08537 A (CIBA GEIGY AG ; BIZE ALINE (CH); ZAMBOUNIS JOHN (CH)) 21 March 1996 (1996-03-21) * example 3 *	2,7	
A	WO 98 32802 A (CIBA GEIGY AG) 30 July 1998 (1998-07-30) * page 23 - page 24 *	4-6	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Place of search THE HAGUE		Date of completion of the search 30 November 2000	Examiner Shade, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 C3 B2 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 81 0848

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-11-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0499011 A	19-08-1992	NONE	
EP 0563009 A	29-09-1993	DE 69318463 D DE 69318463 T JP 6045074 A	18-06-1998 03-09-1998 18-02-1994
JP 02296891 A	07-12-1990	NONE	
JP 05320633 A	03-12-1993	NONE	
JP 09003448 A	07-01-1997	NONE	
EP 0133156 A	13-02-1985	CA 1230341 A DE 3484782 D JP 1758542 C JP 4042431 B JP 60035056 A US 4585878 A US 4666455 A	15-12-1987 14-08-1991 20-05-1993 13-07-1992 22-02-1985 29-04-1986 19-05-1987
EP 0353184 A	31-01-1990	DE 58907880 D JP 3076557 B JP 11344817 A JP 2088579 A JP 3076346 B KR 9711391 B US 5973146 A	21-07-1994 14-08-2000 14-12-1999 28-03-1990 14-08-2000 10-07-1997 26-10-1999
EP 0811625 A	10-12-1997	BR 9703467 A CA 2206756 A CN 1171402 A JP 10081687 A US 5919945 A US 5840907 A US 5786487 A US 5785750 A	06-10-1998 05-12-1997 28-01-1998 31-03-1998 06-07-1999 24-11-1998 28-07-1998 28-07-1998
WO 9825927 A	18-06-1998	AU 5752098 A EP 0944632 A US 5969154 A	03-07-1998 29-09-1999 19-10-1999
WO 9608537 A	21-03-1996	AU 3562595 A	29-03-1996
WO 9832802 A	30-07-1998	AU 6210998 A EP 0968250 A	18-08-1998 05-01-2000

EP 01 087 006 A1

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

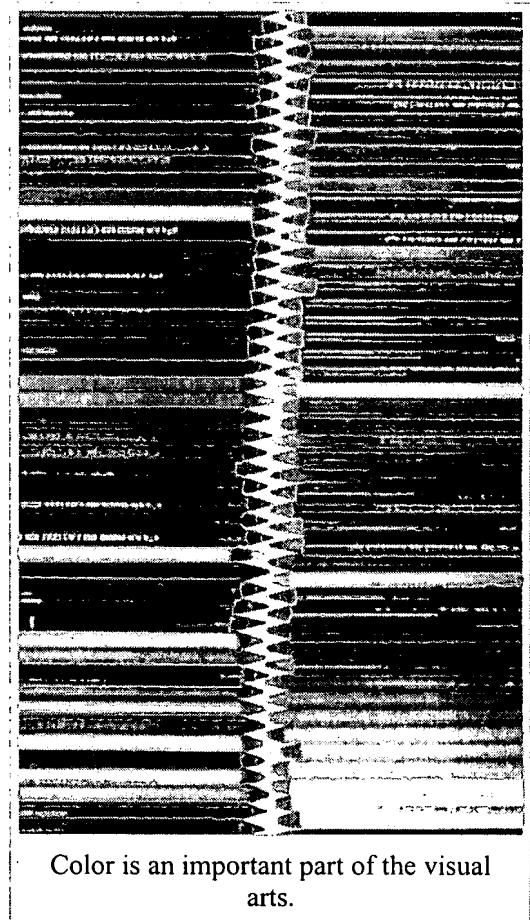
Color

From Wikipedia, the free encyclopedia

Color or **colour** (see spelling differences) is the visual perceptual property corresponding in humans to the categories called *red*, *yellow*, *white*, etc. Color derives from the spectrum of light (distribution of light energy versus wavelength) interacting in the eye with the spectral sensitivities of the light receptors. Color categories and physical specifications of color are also associated with objects, materials, light sources, etc., based on their physical properties such as light absorption, reflection, or emission spectra.

Typically, only features of the composition of light that are detectable by humans (wavelength spectrum from 400 nm to 700 nm, roughly) are included, thereby objectively relating the psychological phenomenon of color to its physical specification. Because perception of color stems from the varying sensitivity of different types of cone cells in the retina to different parts of the spectrum, colors may be defined and quantified by the degree to which they stimulate these cells. These physical or physiological quantifications of color, however, do not fully explain the psychophysical perception of color appearance.

The science of color is sometimes called *chromatics*. It includes the perception of color by the human eye and brain, the origin of color in materials, color theory in art, and the physics of electromagnetic radiation in the visible range (that is, what we commonly refer to simply as *light*).



Contents

- 1 Physics of color
 - 1.1 Spectral colors
 - 1.2 Color of objects
- 2 Color perception
 - 2.1 Development of theories of color vision
 - 2.2 Color in the eye
 - 2.3 Color in the brain
 - 2.4 Nonstandard color perception
 - 2.4.1 Color deficiency
 - 2.4.2 Tetrachromacy
 - 2.4.3 Synesthesia
 - 2.5 Afterimages
 - 2.6 Color constancy
 - 2.7 Color naming

- 3 Associations
- 4 Health effects
- 5 Measurement and reproduction of color
 - 5.1 Relation to spectral colors
 - 5.2 Pigments and reflective media
 - 5.3 Structural color
 - 5.4 Additional terms
- 6 See also
- 7 References
- 8 External links and sources

Physics of color

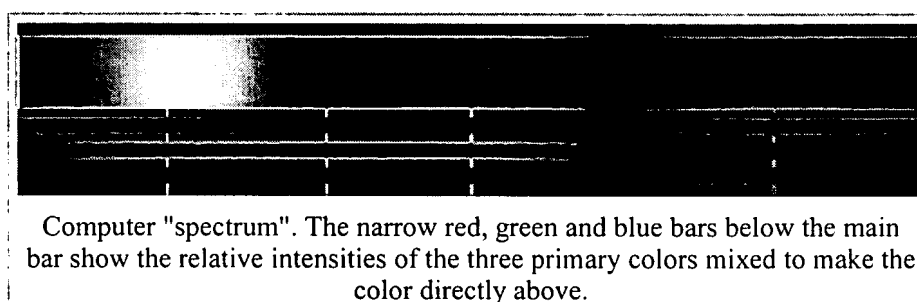
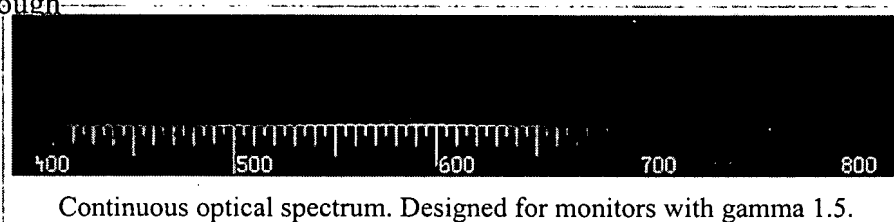
Electromagnetic radiation is characterized by its wavelength (or frequency) and its intensity. When the wavelength is within the visible spectrum (the range of wavelengths humans can perceive, approximately from 380 nm to 740 nm), it is known as "visible light."

Most light sources emit light at many different wavelengths; a source's *spectrum* is a distribution giving its intensity at each wavelength. Although the spectrum of light arriving at the eye from a given direction determines the color sensation in that direction, there are many more possible spectral combinations than color sensations. In fact, one may formally define a color as a class of spectra that give rise to the same color sensation, although such classes would vary widely among different species, and to a lesser extent among individuals within the same species. In each such class the members are called *metamers* of the color in question.

Spectral colors

The colors of the visible light spectrum^[1]

color	wavelength interval	frequency interval
red	~ 630–700 nm	~ 480–430 THz
orange	~ 590–630 nm	~ 510–480 THz
yellow	~ 560–590 nm	~ 540–510 THz
green	~ 490–560 nm	~ 610–540 THz
blue	~ 450–490 nm	~ 670–610 THz
violet	~ 400–450 nm	~ 750–670 THz



Color, wavelength, frequency and energy of light

Color	λ_{nm}	ν /10 ¹⁴ Hz	ν_b /10 ⁴ cm ⁻¹	E /eV	$E/\text{kJ mol}^{-1}$
-------	-----------------------	----------------------------------	---	------------	------------------------

The familiar colors of the rainbow in the spectrum – named for the Latin word for *appearance* or *apparition* by Isaac Newton in 1671 – include all those colors that can be produced by visible light of a single wavelength only, the *pure spectral* or *monochromatic* colors. The table at right shows approximate frequencies (in terahertz) and wavelengths (in nanometers) for various pure spectral colors. The wavelengths are measured in vacuum (see refraction).

Infrared	>1000	<3.00	<1.00	<1.24	<120
Red	700	4.28	1.43	1.77	171
Orange	620	4.84	1.61	2.00	193
Yellow	580	5.17	1.72	2.14	206
Green	530	5.66	1.89	2.34	226
Blue	470	6.38	2.13	2.64	254
Violet	420	7.14	2.38	2.95	285
Near ultraviolet	300	10.0	3.33	4.15	400
Far ultraviolet	<200	>15.0	>5.00	>6.20	>598

The color table should not be interpreted as a definitive list – the pure spectral colors form a continuous spectrum, and how it is divided into distinct colors is a matter of culture, taste, and language. A common list identifies six main bands: red, orange, yellow, green, blue, and violet. Newton's conception included a seventh color, indigo, between blue and violet – but most people do not distinguish it, and most color scientists do not recognize it as a separate color; it is sometimes designated as wavelengths of 420–440 nm.

The *intensity* of a spectral color may alter its perception considerably; for example, a low-intensity orange-yellow is brown, and a low-intensity yellow-green is olive-green.

As discussed in the section on color vision, a light source need not actually be of one single wavelength to be perceived as a pure spectral color.

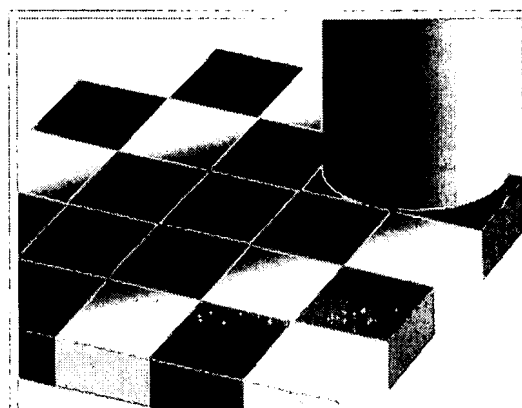
For discussion of non-spectral colors, see below.

Color of objects

The color of an object depends both on physics and on perception. Physically, surfaces can be said to have the color of the light reflecting off them, which depends on the spectrum of the incident illumination and on the reflectance spectrum of the surface, as well as potentially on the lighting and viewing angles. However, a viewer's perception of the object color depends not only on the reflected light spectrum, but also on a host of contextual cues, such that an object's color tends to be perceived as relatively constant, that is, relatively independent of the lighting spectrum, viewing angle, etc. This effect is known as color constancy.

Some generalizations of the physics can be drawn, neglecting perceptual effects for now:

- Light arriving at an opaque surface is either reflected "specularly" (that is, in the manner of a mirror), scattered (that is, reflected with diffuse scattering), or



The orange disk and the brown disk have exactly the same objective color, and are in identical gray surrounds; based on context differences, humans perceive the squares as having different reflectances, and may interpret the colors as different color categories; see same color illusion.

absorbed – or some combination of these.

- Opaque objects that do not reflect specularly (which tend to have rough surfaces) have their color determined by which wavelengths of light they scatter more and which they scatter less (with the light that is not scattered being absorbed). If objects scatter all wavelengths, they appear white. If they absorb all wavelengths, they appear black.
- Opaque objects that specularly reflect light of different wavelengths with different efficiencies look like mirrors tinted with colors determined by those differences. An object that reflects some fraction of impinging light and absorbs the rest may look black but also be faintly reflective; examples are black objects coated with layers of enamel or lacquer.
- Objects that transmit light are either *translucent* (scattering the transmitted light) or *transparent* (not scattering the transmitted light). If they also absorb (or reflect) light of varying wavelengths differentially, they appear tinted with a color determined by the nature of that absorption (or that reflectance).
- Objects may emit light that they generate themselves, rather than merely reflecting or transmitting light. They may do so because of their elevated temperature (they are then said to be *incandescent*), as a result of certain chemical reactions (a phenomenon called *chemoluminescence*), or for other reasons (see the articles Phosphorescence and List of light sources).
- Objects may absorb light and then as a consequence emit light that has different properties. They are then called *fluorescent* (if light is emitted only while light is absorbed) or *phosphorescent* (if light is emitted even after light ceases to be absorbed; this term is also sometimes loosely applied to light emitted due to chemical reactions).

For further treatment of the color of objects, see structural color, below.

To summarize, the color of an object is a complex result of its surface properties, its transmission properties, and its emission properties, all of which factors contribute to the mix of wavelengths in the light leaving the surface of the object. The perceived color is then further conditioned by the nature of the ambient illumination, and by the color properties of other objects nearby, via the effect known as color constancy and via other characteristics of the perceiving eye and brain.

Color perception

Development of theories of color vision

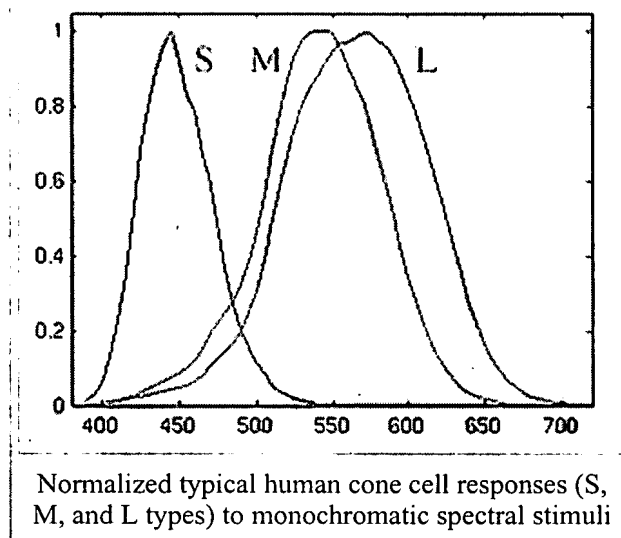
Main article: Color theory

Although Aristotle and other ancient scientists had already written on the nature of light and color vision, it was not until Newton that light was identified as the source of the color sensation. In 1810, Goethe published his comprehensive *Theory of Colors*. In 1801 Thomas Young proposed his trichromatic theory, based on the observation that any color could be matched with a combination of three lights. This theory was later refined by James Clerk Maxwell and Hermann von Helmholtz. As Helmholtz puts it, "the principles of Newton's law of mixture were experimentally confirmed by Maxwell in 1856. Young's theory of color sensations, like so much else that this marvellous investigator

achieved in advance of his time, remained unnoticed until Maxwell directed attention to it."^[2]

At the same time as Helmholtz, Ewald Hering developed the opponent process theory of color, noting that color blindness and afterimages typically come in opponent pairs (red-green, blue-yellow, and black-white). Ultimately these two theories were synthesized in 1957 by Hurvich and Jameson, who showed that retinal processing corresponds to the trichromatic theory, while processing at the level of the lateral geniculate nucleus corresponds to the opponent theory.^[3]

In 1931, an international group of experts known as the Commission Internationale d'Eclairage (CIE) developed a mathematical color model, which mapped out the space of observable colors and assigned a set of three numbers to each.



Color in the eye

The ability of the human eye to distinguish colors is based upon the varying sensitivity of different cells in the retina to light of different wavelengths. The retina contains three types of color receptor cells, or cones. One type, relatively distinct from the other two, is most responsive to light that we perceive as violet, with wavelengths around 420 nm. (Cones of this type are sometimes called *short-wavelength cones*, *S cones*, or, misleadingly, *blue cones*.) The other two types are closely related genetically and chemically. One of them (sometimes called *long-wavelength cones*, *L cones*, or, misleadingly, *red cones*) is most sensitive to light we perceive as yellowish-green, with wavelengths around 564 nm; the other type (sometimes called *middle-wavelength cones*, *M cones*, or misleadingly, *green cones*) is most sensitive to light perceived as green, with wavelengths around 534 nm.

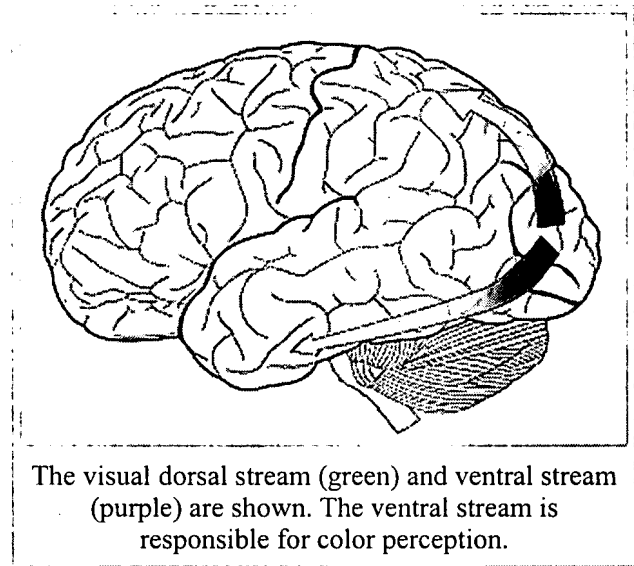
Light, no matter how complex its composition of wavelengths, is reduced to three color components by the eye. For each location in the visual field, the three types of cones yield three signals based on the extent to which each is stimulated. These values are sometimes called *tristimulus values*.

The response curve as a function of wavelength for each type of cone is illustrated above. Because the curves overlap, some tristimulus values do not occur for any incoming light combination. For example, it is not possible to stimulate *only* the mid-wavelength/"green" cones; the other cones will inevitably be stimulated to some degree at the same time. The set of all possible tristimulus values determines the human *color space*. It has been estimated that humans can distinguish roughly 10 million different colors.

The other type of light-sensitive cell in the eye, the rod, has a different response curve. In normal situations, when light is bright enough to strongly stimulate the cones, rods play virtually no role in vision at all.^[4] On the other hand, in dim light, the cones are understimulated leaving only the signal from the rods, resulting in a monochromatic response. (Furthermore, the rods are barely sensitive to light in the "red" range.) In certain conditions of intermediate illumination, the rod response and a weak cone response can together result in color discriminations not accounted for by cone responses alone.

Color in the brain

While the mechanisms of color vision at the level of the retina are well-described in terms of tristimulus values (see above), color processing after that point is organized differently. A dominant theory of color vision proposes that color information is transmitted out of the eye by three opponent processes, or opponent channels, each constructed from the raw output of the cones: a red-green channel, a blue-yellow channel and a black-white "luminance" channel. This theory has been supported by neurobiology, and accounts for the structure of our subjective color experience. Specifically, it explains why we cannot perceive a "reddish green" or "yellowish blue," and it predicts the color wheel: it is the collection of colors for which at least one of the two color channels measures a value at one of its extremes.



The exact nature of color perception beyond the processing already described, and indeed the status of color as a feature of the perceived world or rather as a feature of our *perception* of the world, is a matter of complex and continuing philosophical dispute (see qualia).

Nonstandard color perception

Color deficiency

If one or more types of a person's color-sensing cones are missing or less responsive than normal to incoming light, that person can distinguish fewer colors and is said to be *color deficient* or *color blind* (though this latter term can be misleading; almost all color deficient individuals can distinguish at least some colors). Some kinds of color deficiency are caused by anomalies in the number or nature of cones in the retina. Others (like *central* or *cortical achromatopsia*) are caused by neural anomalies in those parts of the brain where visual processing takes place.

Tetrachromacy

While most humans are *trichromatic* (having three types of color receptors), many animals, known as *tetrachromats*, have four types. These include some species of spiders, most marsupials, birds, reptiles, and many species of fish. Other species are sensitive to only two axes of color or do not perceive color at all; these are called *dichromats* and *monochromats* respectively. A distinction is made between *retinal tetrachromacy* (having four pigments in cone cells in the retina, compared to three in trichromats) and *functional tetrachromacy* (having the ability to make enhanced color discriminations based on that retinal difference). As many as a half of all women, but only a small percentage of men, are retinal tetrachromats. The phenomenon arises when an individual receives two slightly different copies of the gene for either the medium- or long-wavelength cones (which are carried on the x-chromosome). For some of these retinal tetrachromats, color discriminations are enhanced, making them functional

tetrachromats.^[5]

Synesthesia

In certain forms of synesthesia, perceiving letters and numbers (grapheme → color synesthesia) or hearing musical sounds (music → color synesthesia) will lead to the unusual additional experiences of seeing colors. Behavioral and functional neuroimaging experiments have demonstrated that these color experiences lead to changes in behavioral tasks and lead to increased activation of brain regions involved in color perception, thus demonstrating their reality, and similarity to real color percepts, albeit evoked through a non-standard route.

Afterimages

After exposure to strong light in their sensitivity range, photoreceptors of a given type become desensitized. For a few seconds after the light ceases, they will continue to signal less strongly than they otherwise would. Colors observed during that period will appear to lack the color component detected by the desensitized photoreceptors. This effect is responsible for the phenomenon of afterimages, in which the eye may continue to see a bright figure after looking away from it, but in a complementary color.

Afterimage effects have also been utilized by artists, including Vincent van Gogh.

Color constancy

There is an interesting phenomenon which occurs when an artist uses a limited color palette: the eye tends to compensate by seeing any grey or neutral color as the color which is missing from the color wheel. E.g., in a limited palette consisting of red, yellow, black and white, a mixture of yellow and black will appear as a variety of green, a mixture of red and black will appear as a variety of purple, and pure grey will appear bluish.

The trichromatic theory discussed above is strictly true only if the whole scene seen by the eye is of one and the same color, which of course is unrealistic. In reality, the brain compares the various colors in a scene, in order to eliminate the effects of the illumination. If a scene is illuminated with one light, and then with another, as long as the difference between the light sources stays within a reasonable range, the colors of the scene will nevertheless appear constant to us. This was studied by Edwin Land in the 1970s and led to his retinex theory of color constancy.

Color naming

Colors vary in several different ways, including hue (red vs. orange vs. blue), saturation, brightness, and gloss. Some color words are derived from the name of an object of that color, such as "orange" or "salmon", while others are abstract, like "red".

Different cultures have different terms for colors, and may also assign some color names to slightly different parts of the spectrum: for instance, the Chinese character 青 (rendered as *qīng* in Mandarin and *ao* in Japanese) has a meaning that covers both blue and green; blue and green are traditionally considered shades of "青."

In the 1969 study *Basic Color Terms: Their Universality and Evolution*, Brent Berlin and Paul Kay describe a pattern in naming "basic" colors (like "red" but not "red-orange" or "dark red" or "blood red", which are "shades" of red). All languages that have two "basic" color names distinguish dark/cool colors from bright/warm colors. The next colors to be distinguished are usually red and then blue or green. All languages with six "basic" colors include black, white, red, green, blue and yellow. The pattern holds up to a set of twelve: black, grey, white, pink, red, orange, yellow, green, blue, purple, brown, and azure (distinct from blue in Russian and Italian but not English).

Associations

Individual colors have a variety of cultural associations such as national colors (in general described in individual color articles and color symbolism). The field of color psychology attempts to identify the effects of color on human emotion and activity. Chromotherapy is a form of alternative medicine attributed to various Eastern traditions.

Health effects

When the color spectrum of artificial lighting is mismatched to that of sunlight, material health effects may arise including increased incidence of headache. This phenomenon is often coupled with adverse effects of over-illumination, since many of the same interior spaces that have color mismatch also have higher light intensity than desirable for the task being conducted in that space.

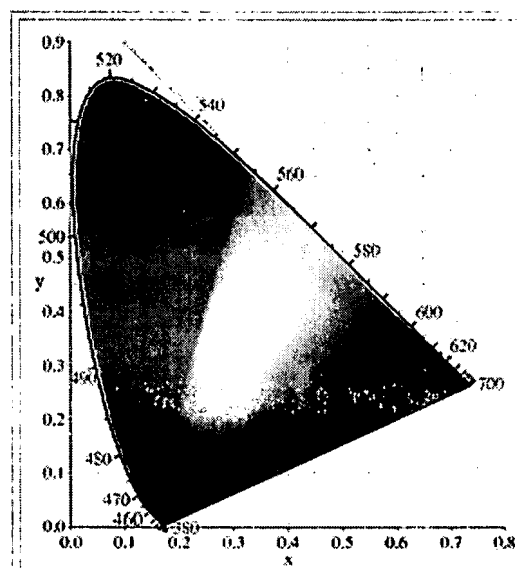
Measurement and reproduction of color

Relation to spectral colors

Most light sources are mixtures of various wavelengths of light. However, many such sources can still have a spectral color insofar as the eye cannot distinguish them from monochromatic sources. For example, most computer displays reproduce the spectral color orange as a combination of red and green light; it appears orange because the red and green are mixed in the right proportions to allow the eye's red and green cones to respond the way they do to orange.

A useful concept in understanding the perceived color of a non-monochromatic light source is the dominant wavelength, which identifies the single wavelength of light which produces a sensation most similar to the light source. Dominant wavelength is roughly akin to hue.

Of course, there are many color perceptions that by definition cannot be pure spectral colors due to desaturation or because they are purples (mixtures of red and violet light, from opposite ends of the spectrum). Some examples of



The CIE 1931 color space chromaticity diagram. The outer curved boundary is the spectral (or monochromatic) locus, with wavelengths shown in nanometers. Note that the colors depicted depend on the

necessarily non-spectral colors are the achromatic colors (black, gray and white) and colors such as pink, tan, and magenta.

color space of the device on which you are viewing the image, and therefore may not be a strictly accurate representation of the color at a particular position, and especially not for monochromatic colors.

Two different light spectra which have the same effect on the three color receptors in the human eye will be perceived as the same color. This is exemplified by the white light that is emitted by fluorescent lamps, which typically has a spectrum consisting of a few narrow bands, while daylight has a continuous spectrum. The human eye cannot tell the difference between such light spectra just by looking into the light source, although reflected colors from objects can look different. (This is often exploited e.g. to make fruit or tomatoes look more brightly red in shops.)

Similarly, most human color perceptions can be generated by a mixture of three colors called *primaries*. This is used to reproduce color scenes in photography, printing, television and other media. There are a number of methods or color spaces for specifying a color in terms of three particular primary colors. Each method has its advantages and disadvantages depending on the particular application.

No mixture of colors, though, can produce a fully pure color perceived as completely identical to a spectral color, although one can get very close for the longer wavelengths, where the chromaticity diagram above has a nearly straight edge. For example, mixing green light (530 nm) and blue light (460 nm) produces cyan light that is slightly desaturated, because response of the red color receptor would be greater to the green and blue light in the mixture than it would be to a pure cyan light at 485 nm that has the same intensity as the mixture of blue and green.

Because of this, and because the *primaries* in color printing systems generally are not pure themselves, the colors reproduced are never perfectly saturated colors, and so spectral colors cannot be matched exactly. However, natural scenes rarely contain fully saturated colors, thus such scenes can usually be approximated well by these systems. The range of colors that can be reproduced with a given color reproduction system is called the gamut. The CIE chromaticity diagram can be used to describe the gamut.

Another problem with color reproduction systems is connected with the acquisition devices, like cameras or scanners. The characteristics of the color sensors in the devices are often very far from the characteristics of the receptors in the human eye. In effect, acquisition of colors that have some special, often very "jagged," spectra caused for example by unusual lighting of the photographed scene can be relatively poor.

Species that have color receptors different from humans, e.g. birds that may have four receptors, can differentiate some colors that look the same to a human. In such cases, a color reproduction system 'tuned' to a human with normal color vision may give very inaccurate results for the other observers.

The next problem is different color response of different devices. For color information stored and transferred in a digital form, color management technique based on color profiles attached to color data and to devices with different color response helps to avoid deformations of the reproduced colors. The technique works only for colors in gamut of the particular devices, e.g. it can still happen that your monitor is not able to show you real color of your goldfish even if your camera can receive and store the color information properly and vice versa.

Pigments and reflective media

Pigments are chemicals that selectively absorb and reflect different spectra of light. When a surface is painted with a pigment, light hitting the surface is reflected, minus some wavelengths. This subtraction of wavelengths produces the appearance of different colors. Most paints are a blend of several chemical pigments, intended to produce a reflection of a given color.

Pigment manufacturers assume the source light will be white, or of roughly equal intensity across the spectrum. If the light isn't a pure white source (as in the case of nearly all forms of artificial lighting), the resulting spectrum will appear a slightly different color. Red paint, viewed under blue light, may appear black. Red paint is red because it reflects only the red components of the spectrum. Blue light, containing none of these, will create no reflection from red paint, creating the appearance of black.

Structural color

Structural colors are colors caused by interference effects rather than by pigments. Color effects are produced when a material is scored with fine parallel lines, formed of a thin layer or of two or more parallel thin layers, or otherwise composed of microstructures on the scale of the color's wavelength. If the microstructures are spaced randomly, light of shorter wavelengths will be scattered preferentially to produce Tyndall effect colors: the blue of the sky, the aerogel of opals, and the blue of human irises. If the microstructures are aligned in arrays, for example the array of pits in a CD, they behave as a diffraction grating: the grating reflects different wavelengths in different directions due to interference phenomena, separating mixed "white" light into light of different wavelengths. If the structure is one or more thin layers then it will reflect some wavelengths and transmit others, depending on the layers' thickness.

Structural color is responsible for the blues and greens of the feathers of many birds (the blue jay, for example), as well as certain butterfly wings and beetle shells. Variations in the pattern's spacing often give rise to an iridescent effect, as seen in peacock feathers, soap bubbles, films of oil, and mother of pearl, because the reflected color depends upon the viewing angle. Peter Vukusic has carried out research in butterfly wings and beetle shells using electron micrography, and has since helped develop a range of "photonic" cosmetics using structural color.

Structural color is studied in the field of thin-film optics. A layman's term that describes particularly the most ordered structural colors is iridescence.

Additional terms

- Hue: the color's direction from white, for example in the CIE chromaticity diagram.
- Saturation: how "intense" or "concentrated" a color is; also known as chroma or purity.
- Value: how light or dark a color is.
- Tint: a color made lighter by adding white.
- Shade: a color made darker by adding black.

See also

- Chromophore
- Color blindness
- Color psychology

- Color scheme
- Color Symbolism
- Color temperature
- Color theory
- Dichromatism (the color of a substance changes by changing the layer thickness)
- Goethe's *Theory of Colors*
- Kruithof curve
- List of colors
- Metamerism
- Political color
- Political Colors and emblems for parties
- Qualia
- Synesthesia
- The International Commission on Illumination defines colors and color spaces
- Thermochromics
- Tincture (heraldry). The colors in heraldry.
- Web colors

References

1. ^ Craig F. Bohren (2006). *Fundamentals of Atmospheric Radiation: An Introduction with 400 Problems* (http://books.google.com/books?vid=ISBN3527405038&id=1oDOWr_yueIC&pg=PA214&lpg=PA214&ots=Jrfi5sPBhk&dq=indigo+spectr-2007&sig=Rm2xP5mIgyGJ1a1phfAt65QSf0I#PPA214,M1). Wiley-VCH. ISBN 3527405038.
2. ^ Hermann von Helmholtz, *Physiological Optics -- The Sensations of Vision*, 1866, as translated in *Sources of Color Science*, David L. MacAdam, ed., Cambridge: MIT Press, 1970.
3. ^ Palmer, S.E. (1999). *Vision Science: Photons to Phenomenology*. Cambridge, MA: MIT Press. ISBN 0-262-16183-4
4. ^ "Under well-lit viewing conditions (photopic vision), cones...are highly active and rods are inactive." Hirakawa, K., and Parks, T.W. (2005). "*Chromatic Adaptation and White-Balance Problem* (<http://www.accidentalmark.com/research/papers/Hirakawa05WBICIP.pdf>)" (PDF). IEEE ICIP.
5. ^ Jameson, K. A., Highnote, S. M., & Wasserman, L. M. (2001). "Richer color experience in observers with multiple photopigment opsin genes: (<http://www.klab.caltech.edu/cns186/papers/Jameson01.pdf>)" (PDF). *Psychonomic Bulletin and Review* 8 (2): 244–261.

External links and sources

- Online papers on color and color experience (<http://consc.net/online1.html#color>), by various authors, compiled by David Chalmers
- International Color Consortium (<http://www.color.org/>)
- Munsell Color Science Laboratory (<http://www.cis.rit.edu/mcsl/>)
- NIST Reference on International System of Units (SI) (<http://physics.nist.gov/cuu/Units/>)
- Standard viewing conditions (http://www.ipa.org/bulletin/articles/view_cond.php3)
- Bruce Lindbloom web page (<http://www.brucelindbloom.com/>)
- Mark Fairchild web page (<http://www.cis.rit.edu/fairchild/>)
- Charles Poynton web page (<http://www.poynton.com/>)
- Comparative Article examining Goethean and Newtonian Color (<http://www.physicstoday.org/vol-55/iss-7/p43.html>)
- Kruithof curve citation (<http://palimpsest.stanford.edu/waac/wn/wn21/wn21-3/wn21-308.html>)
- Article by technical lighting manufacturer on rod/cone vision, with cites to literature (<http://www.soluxtli.com/edu13.htm>)

- Stanford Encyclopedia of Philosophy entry (<http://plato.stanford.edu/entries/color/>)
- Why are things colored? (<http://webexhibits.org/causesofcolor/>)
- Why Should Engineers and Scientists Be Worried About Color? (<http://www.research.ibm.com/people/l/lloyd/color/color.HTM>)
- Color, Contrast & Dimension in News Design (<http://poynterextra.org/cp/colorproject/color.html>)

Retrieved from "<http://en.wikipedia.org/wiki/Color>"

Categories: Semi-protected | All articles with unsourced statements | Articles with unsourced statements since February 2007 | Articles with unsourced statements since March 2007 | Color | Image processing | Vision

- This page was last modified 19:31, 10 August 2007.
- All text is available under the terms of the GNU Free Documentation License. (See **Copyrights** for details.) Wikipedia® is a registered trademark of the Wikimedia Foundation, Inc., a US-registered 501(c)(3) tax-deductible nonprofit charity.